Computational Study of Electrochemical Water Oxidation of Manganese Complex

By

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STATEMENT

I hereby inform that the matter presented in this dissertation entitled "**Computational Study of Electrochemical Water Oxidation of Manganese Complex** " is based on the results of investigation carried out by me at School of Chemical Sciences, Goa University under the supervision of Dr. Vivekanand V. Gobre and the same has not been submitted elsewhere for the award of M.Sc. degree.

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CERTIFICATE

This is to certify that dissertation entitled "**Computational Study of Electrochemical Water Oxidation of Manganese Complex** " is a bonafide work carried out by Miss. Aisha Shaikh under my supervision in partial fulfillment of requirements for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

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CERTIFICATE BY DEAN

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ABSTRACT

Endeavouring for new solar fuels, the water oxidation reaction currently is considered to be a bottleneck as it is a very promising technology to convert solar energy to chemical energy. It is a favourable mechanisation for supplying clean and sustainable fuel by production of hydrogen. The oxidation of water is thermodynamically unfavorable with a relatively large energy demand and is therefore quite challenging to accomplish. Hence, enormous efforts are being pursued to develop efficient water-oxidising catalysts at potentials close to thermodynamic limit.

In nature, Manganese plays a crucial role in oxidation of water in photosynthesis process; as a result of which, the design and synthesis of biomimetic Manganese complexes to catalyze oxygen evolution is an appealing goal. Recently, a mononuclear Mn complex **1** $[Mn(N_3Py_2)H_2O]^{2+}$ was reported to catalyse electrocatalytic water oxidation in basic aqueous solution. Density functional calculations have been performed to elucidate the mechanism of water oxidation promoted by this catalyst.

The calculations showed that **1** can readily lose two protons and two electrons with the production of **2** $[LMn^{IV}{=}O]^{2+}$, which then undergoes electron transfer processes to form **3** $[LMn^{V}{=}O]^{3+}$. A water molecule initiates a nucleophillic attack on complex **3** and leads to formation of complex **4** $[LMn^{III}\text{-}OOH]^{2+}$. There is a loss of proton and an electron to form complex **5** $[LMn^{IV}\text{-}OO]^{2+}$. Upon addition of water molecule to complex **5**, the Mn-Oxo bond breaks to evolve O_2 molecule and complex **1** gets regenerated with attachment of aqua ligand. Moreover, redox-potential leveling, proton removal, and O-O bond formation mechanism are discussed.

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Contents

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Introduction

Increased interest in conversion of solar energy into storable fuel has escalated research efforts with respect to artificial water splitting [1]. Electrochemical splitting of water to hydrogen and oxygen shows signs of success to generate hydrogen fuel [2]. In water splitting, there is oxidation of water to oxygen (O_2) and the resulting protons and electrons reduce to form hydrogen (H_2). Thus, the first step of water splitting is called water oxidation[1]. However, due to kinetic and thermodynamic barriers, the oxygen-evolution reaction (OER) is the most challenging half-reaction in water oxidation. Hence, there is a need to develop efficient water-oxidising catalysts, which can lower the overpotential of the oxidation-half reaction. Since Mn_4CaO_5 cluster in photosystem II is the only natural system that demonstrates water oxidation, manganese-based compounds have attracted tremendous attention [3]. Manganese is an earth-abundant, environmentally friendly and low-cost element. Interesting properties of manganese oxides have made them attractive materials in various catalytic applications. Also, mimicking the OER is an attracting area of research as it has various applications such as fuel cells, metal-air batteries, catalytic reactions, industrial waste treatments, etc [4].

Water oxidation catalyzed by mononuclear ruthenium and Iridium complexes have been reported, but their low natural abundances make them costlier. Thus, synthesizing an effective OER catalyst by prudent selection of metal with proper ligands is a supreme goal of the researchers working in the field of water splitting. Therefore, attempts are made to synthsize manganese complexes which can catalyze oxidation of water[1]. There have been

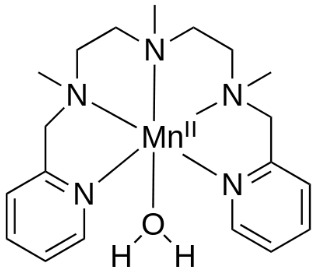

Figure 1.1: Structure of Mn complex-H_2O

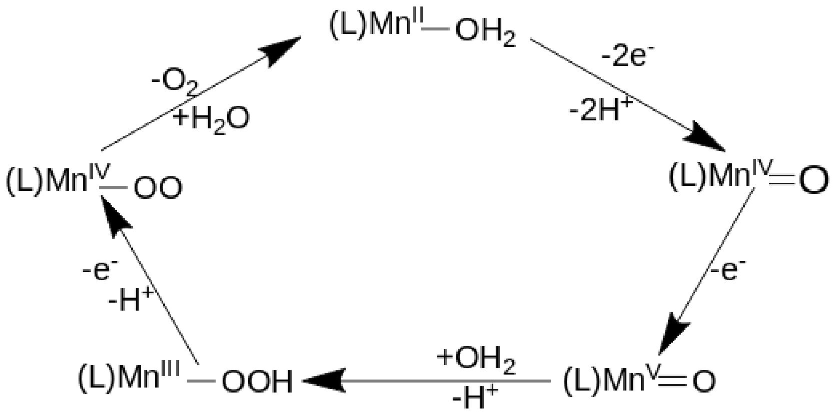

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Figure 1.2: Proposed mechanism of water oxidation

considerable efforts to find efficient manganese complexes as homogenous or heterogeneous water-oxidizing catalysts [5]. Non-heme Mn catalysts are preferred due to their high solubility in aqueous and non-aqueous electrolytes, providing easy way to predict reaction pathway. They are also easily synthesizable, tunable, reproducible and owe good mechanistic probes [6]. Recently, a mononuclear Mn complex $[Mn(N_3Py_2)H_2O]^{2+}$ was reported to catalyse electrocatalytic water oxidation in basic aqueous solution. The rate of water oxidation shows first order dependence on concentration of Mn complex and pH of reaction medium[7]. Hence there was a need to perform DFT calculations inorder to support plausibility of proposed mechanism. It uses quantum and classical mechanics to systematically investigate and comprehend the proposed mechanism of water oxidation[8].

The investigation begins with hexa-coordinated Mn^{II} complex **1** $[LMn^{II}(H_2O)]^{2+}$ $(L=N_3Py_2)$, the ligand framework of which is composed of three amines, two pyridines and one aqua ligand. The high spin sextet Mn^{II} complex **1** undergoes oxidation with release of two protons and forms a d^3 system **2** $[LMn^{IV}=O]^{2+}$. This quartet complex undergoes oxidation by loss of an electron to form triplet complex **3** $[LMn^{V}=O]^{3+}$. In formal Mn(V) state, a water molecule initiates a nucleophillic attack on complex **3** and leads to oxo-oxo coupling which thereby leads to formation of quintet complex **4** $[LMn^{III}\text{-}OOH]^{2+}$ in which the two oxygen atoms have opposite spins. Then there is oxidation from d^4 to d^3 system by loss of proton and an electron to form complex **5** $[LMn^{IV}\text{-}OO]^{2+}$. Upon addition of water molecule to complex **5**, the Mn-Oxo bond breaks to evolve O_2 molecule and complex **1** gets regenerated with attachment of aqua ligand [9].

2

Theoretical methods

This chapter intends to give brief explaination on some concepts of Computational Chemistry and the theoretical methods used in this dissertation for the calculation of transition states involved in electrochemical water oxidation by manganese complex. Theoretical Chemistry is the subfield of Chemistry, which is a combination of mathematical methods and fundamental laws of physics inorder to study chemical processes[10]. It uses quantum and classical mechanics to systematically investigate chemical reactions[8]. Implementation of mathematical methods on a computer gives rise to Computational Chemistry[10].

Computational chemistry is a set of techniques that uses computer simulations for investigating chemical problems such as molecular geometry, energies of molecules, chemical reactivity, physical properties, IR, UV, NMR spectra, etc. The main tools of computational chemistry include molecular mechanics, ab initio calculations, semi empirical methods, density functional theory and molecular dynamics. These tools aim at solving electronic many-body problem using well defined principles which are briefly explained in this chapter. The interested reader may obtain a better understanding of the methods discussed in references[8].

Molecular mechanics is the key to theoretical Chemistry and is widely used as a predictive tool in structure and reactivity studies of organic and organometallic systems. Ab initio calculations and semiempirical calculations are based on the Schrödinger equation. The geometries, energies, frequencies of transition states, electron distribution in molecular species can be determined from quantum mechanical calculations. Quantum mechanical calculations also provide information about reaction meachanisms and product distribution. Density functional calculation allows prediction of dipole moment, charge distribution, bond orders and shapes of molecular orbitals. Consequently, molecular dynamics calculations apply the laws of motion to molecules allowing to simulate the motion of molecules in presence of other molecules [10].

1 Background of Computational Chemistry

Computational Chemistry is based on work of Schrödinger and Heisenberg. By solving the time-independent Schrödinger equation, Eq.2.1.1,various properties of a molecule can be appropriately determined[11].

$$E\psi = \hat{H}\psi \tag{2.1.1}$$

Nevertheless, Schrödinger equation is limited to systems with only one electron. Hence, to overcome the limitation of Schrödinger equation for many-electron system, Hartree developed self-consistent field (SCF) theory. Hartree's SCF approach places each electron into its own one-electron wavefunction and the product of these individual wavefunctions is used as eigen function in Schrödinger equation. Solving one-electron Schrödinger equation generates new set of wavefunctions which are solved repeatedly until change in energy from one wavefunction to the next is below a certain threshold. However, the wavefunctions being not antisymmetric, violate Pauli-exclusion principle. Therefore, inorder to account for this requirement, Fock expanded Hartree's work by utilizing Slater determinants and led to the development of Hartree-Fock (HF) theory[11].

In 1950s, with the availability of computing technology HF theory became possible, yet the computational cost remained high. In early 1960s, Hohemberg, Kohn and Sham attempted to describe electrons in such a way that did not require evaluation of each pair-wise interaction in many-body wavefunction. They represented electrons as an assembly of non-interacting electrons in an effective potential which could be expressed as the ground-state electron density. This led to formation of density functional theory (DFT). It gained popularity due to its ability to expand the scope of chemical systems without excessive computing power[11].

2 Molecular Mechanics

Molecular mechanics is established on a mathematical model of a molecule as a collection of balls held together by springs. According to this model, due to the resistance offered by the springs in being stretched or bent, the energy of the molecule changes with geometry [12]. The Molecular mechanics model ignores electronic aspects of a molecule. The primary assumption of the molecular mechanics is Born-Oppenheimer approximation, which allows separation of nuclear and electronic motions. Other fundamental assumptions involve additivity and transferability of parameters. Additivity implies that the potential energy of any system can be expressed as a combination of different potentials (bond deformations, electrostatics, dispersion forces etc.). Transferability means that the energy associated with any particular molecular motion is taken to be same for different molecules. The correctness of molecular mechanics force fields depends on the validity of these assumptions[13].

Also, it treats atoms as perfect spheres, the bonds between molecules are treated as springs, potential functions are dependent on experimental parameters like force constants and equilibrium values. This provides a fairly simple calculation which can be extended to huge molecular systems. The functioning of this technique depends on the functional form of energy expression, the data used to parameterize the constants, the technique used to optimize constants from that data and the ability of the user to apply the technique in a way consistent with its strengths and weaknesses [12].

Molecular mechanics is conceptualized to express the energy of a molecule as a function of its resistance towards bond stretching, bond bending, and atom crowding, and also, to utilize this energy equation to find the bond lengths, angles, and dihedral corresponding to the minimum-energy geometry. The molecular mechanics energy expression consists of the sum of simple classical equations which describe various aspects of the molecule, such as bond stretching, bond bending, torsions, electrostatic interactions, van Der Waals forces, and hydrogen bonding.

$$E = \sum_{\text{bonds}} E_{\text{stretch}} + \sum_{\text{angles}} E_{\text{bend}} + \sum_{\text{dihedrals}} E_{\text{torsion}} + \sum_{\text{pairs}} E_{\text{nonbonded}} \tag{2.2.2}$$

where $\mathrm{E}_{\text{stretch}}$, E_{bend}, $\mathrm{E}_{\text{torsion}}$, $\mathrm{E}_{\text{nonbonded}}$ are energy contributions from bond stretching, angle bending, torsional motion around single bonds and interactions between atoms which are nonbonded. Molecular mechanics is advantageous as it requires less of computer than quantum mechanical methods, and also can be applied to large molecules such as proteins. However, its drawbacks include that it is not applicable for electronic properties and is restricted by parameters of equations, i.e. a different force-field is required for different types of atoms [14].

In molecular mechanics, the functional form and parameter sets required to calculate the potential energy of a system of atoms is referred to as a force field. The parameters of energy functions are obtained from experiments or calculations in quantum mechanics. The elementary functional form of potential energy comprises of bonded terms for covalently bonded interactions of atoms, and, nonbonded terms which explain the long-range electrostatics and van der Waals forces. Also, force fields determine a set of parameters for different types of atoms, chemical bonds, dihedral angles, etc [15].

The force fields are classified into classical, polarisable, reactive and coarse-grained. Force fields vary depending upon the number of terms present in the energy expression, the intricacy of these terms and the way in which the constants could be obtained. Different force fields are designed for different purposes and all are implemented in various computer softwares; namely, Assisted model building with energy refinement (AMBER), Chemistry at Harvard macromolecular mechanics (CHARMM), Consistent force field (CFF), Empirical force field (EFF), Gronigen molecular simulation (GROMOS), Optimized potentials for liquid simulation (OPLS), etc [14].

UFF is the most favourable force field available for full periodic table. It is widely used for geometry optimizations, calculations of single point energies, frequencies and to do transition state searches. It can also do calculations with chain and bulk periodicity. However, it lacks to optimize the geometry of lattice vectors and of periodic systems with unit cells lesser than 6 Angstrom.[14].

Chemistry at Harvard macromolecular mechanics (CHARMM) refers to a force field which was devised for proteins and nucleic acids; but it was later extended to a range of biomolecules, molecular dynamics, solvation, crystal packing, vibrational analysis, etc. It allows generating and analysing a wide range of molecular simulations[14]. It also includes polarizable force fields using two approaches; based on the fluctuating charge (FQ) model and on the Drude shell or dispersion oscillator model. It also facilitates free energy perturbation (FEP), quasi-harmonic entropy estimation, correlation analysis, etc [16].

In CHARMM force field the potential energy function is given by

$$
\begin{aligned}
V = \sum_{\text{bonds}} k_b(b-b_o)^2 + \sum_{\text{angles}} k_\theta(\theta-\theta_o)^2 + \sum_{\text{dihedrals}} k_\phi[1+cos(n\phi-\delta)] \\
+ \sum_{\text{impropers}} k_w(w-w_o)^2 + \sum_{\text{Urey-Bradley}} k_u(u-u_o)^2 \\
+ \sum_{\text{nonbonded}} \varepsilon\left[\left(\frac{R_{min_{ij}}}{r_{ij}}\right)^{12} - \left(\frac{R_{min_{ij}}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{\varepsilon r_{ij}} \qquad (2.2.3)
\end{aligned}
$$

V is the intermolecular potential between the two atoms or molecules.

First term: describes bond stretches where k_b is the bond force constant and $b - b_0$ is the distance from equilibrium that the atom has moved. It represents the energy between covalently bonded atoms. It is a harmonic force which is a good approximation near the equilibrium bond length

Second term: describes bond angles where k_θ is the angle force constant and $\theta - \theta_0$ is the angle from equilibrium between three bonded atoms. It represents the energy due to the geometry of electron orbitals involved in covalent bonding.
Third term: accounts for dihedrals where k_ϕ is the dihedral force constant, n is the multiplicity of the function, ϕ is the dihedral angle and δ is the phase shift. It represents the energy for twisting a bond due to bond order and neighboring bonds or lone pairs of electrons. The total torsional energy is expressed as a Fourier series.
Fourth term: accounts for the impropers (out of plane bending) where k_ω is the force constant and $\omega - \omega_0$ is the out of plane angle.
Fifth term: Urey-Bradley component, where k_U is the force constant and U is the distance between the 1,3 atoms in the harmonic potential.
Sixth term: accounts for nonbonded interactions between pairs of atoms (i, j). It represents the non-bonded energy between all atom pairs, which can be decomposed into van der Waals and electrostatic coulomb energies. The van Der Waals energy is calculated using the equilibrium distance $R_{min_{ij}}$ and well depth (ϵ). The nonbonded forces are applicable to atom pairs separated by at least three bonds. The van Der Waals energy is calculated with a standard 12-6 Lennard-Jones potential and the electrostatic energy with a Coulombic potential. In the Lennard-Jones potential, the $R_{min_{ij}}$ term is the distance where the Lennard-Jones potential is minimum[17].

Assisted model building with energy refinement (AMBER) is also a popular forcefield and a molecular mechanics program. It is the functional form used by the family of AMBER force fields for molecular dynamics of biomolecules. It was parameterized specifically for proteins and nucleic acids. AMBER uses only five bonding and non-bonding terms along with a sophisticated electrostatic treatment. Results are very good for proteins and nucleic acids, but can be somewhat erratic for other systems[14].

The chief application of molecular mechanics is in the field of molecular dynamics. It uses force field for calculation of forces that act on each particle and an appropriate integrator to model the dynamics of the particles and predict trajectories. Molecular mechanics is also applied for energy minimization, wherein force field is used for optimization. Moreover, mechanical mechanics potential energy functions have been employed for calculation of binding constants, kinetics of protein folding, to design binding sites, protonation equilibrium, etc[13].

Generally, the functional form of any force field depends on the specific simulation program. The bond and angle terms are described as harmonic potentials. The torsional term is anharmonic[12]. In non-bonded terms van

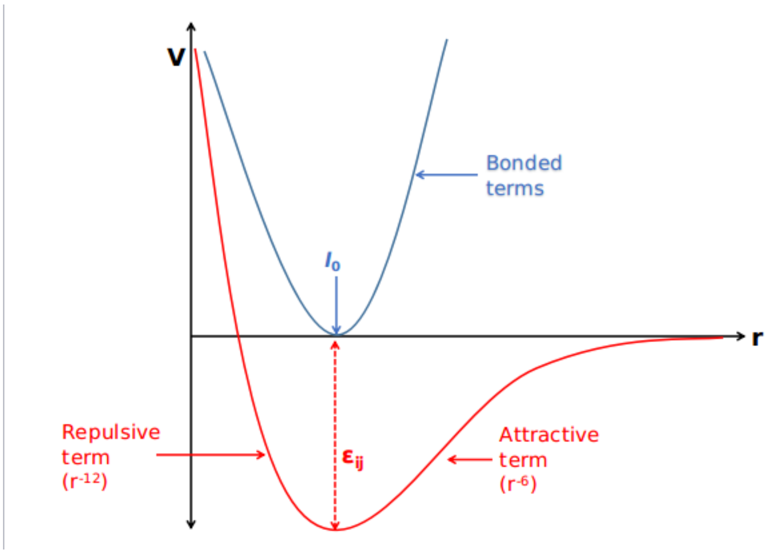

Figure 2.1: Behaviour of different components of force field

Der Waals energies are modeled using 6-12 Lennard-Jones potential, according to which attractive forces fall off with distance as r^{-6} and repulsive forces as r^{-12}, where r is the distance between two atoms. The electrostatic energies are modeled using Coulomb potential[18]. In Lennard-Jones potential, the r^{-12} is the repulsive term and it illustrates Pauli repulsion due to overlap between electron orbitals. The r^{-6} is an attractive term and it explains attraction at long ranges i.e. van Der Waals forces. Upon differentiating the L-J potential with respect to r, we obtain an expression for net intra-molecular forces which may be attractive or repulsive depending on the value of r. Small values of r implies repulsion between molecules[14][13].

Along with the functional form of each energy term, parameters for force constants need to be assigned. The force constants, van Der Waals multipliers, other constant terms; together with the equilibrium bond, angle, dihedral values, atomic masses, radii and energy function collectively define a forcefield. Each forcefield is parametrized to be internally consistent, however these parameters cannot be transferred from one forcefield to another[18].

3 Quantum Mechanics

Quantum mechanics explains the behaviour of electrons and can predict properties of atoms and molecules. The quantum mechanics equations are solved exactly for one electron systems and approximated for multiple electron systems. It studies ground state of individual atoms/molecules and predicts the excited states and transition states occurring in chemical reactions.

3.1 Schrödinger Equation

Schrödinger equation is the foundation of quantum mechanics. It is based on the fundamental postulate that for any chemical system, there exists a wave function, Ψ, and appropriate operators act upon Ψ inorder to yield the observable properties of the system. The Schrödinger equation is expressed as

$$\hat{H}\Psi = E\Psi \tag{2.3.4}$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is wavefunction and E is the energy. This equation is called eigen value equation, wherein, Ψ is called eigen function and E is called eigen value. Since wave function is the square of wavefunction that gives probabilities, the wavefunction is called probability amplitude. The wavefunction Ψ is a function of the electron and nuclear positions. The electron described as a wave, gives the probability of electron positions but cannot predict the location exactly. The wave function must be continuous, single-valued and normalizable inorder to obtain solution of Schrödinger equation[14].

The Hamiltonian operator, $\hat{H}$, operates on wavefuntion to give the total energy. The typical form of the Hamiltonian operator takes into account five contributions to the total energy of a system: the kinetic energies of the electrons and nuclei, the attraction of the electrons to the nuclei, and the interelectronic and internuclear repulsions. In general, the Hamiltonian operator $\hat{H}$ is given by

$$\hat{H} = -\sum_{\mathrm{i}} \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{\mathrm{k}} \frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_{\mathrm{i}}\sum_{\mathrm{k}} \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}} \tag{2.3.5}$$

where i and j run over electrons, k and l run over nuclei, $\hbar$ is Planck's constant divided by 2π, m_e is the mass of the electron, m_k is the mass of nucleus k, ∇^2 is the Laplacian operator, e is the charge on the electron, Z is an atomic number, and r_{ab} is the distance between particles a and b. In Cartesian coordinates, the Laplacian operatotor, ∇^2, is defined as

$$\nabla_i^2 = \frac{\delta^2}{\delta x_i^2} + \frac{\delta^2}{\delta y_i^2} + \frac{\delta^2}{\delta z_i^2} \tag{2.3.6}$$

Hamiltonian operator can be simplified by an approximation called Born-Oppenheimer approximation which is obtained by separation of nuclear and electron motions[18][14].

3.2 Born-Oppenheimer approximation

Born-Oppenheimer illustrates that the nuclei in a molecule are stationary with respect to the electrons as nuclei are much heavier than the electron. Mathematically, the approximation states that the Schrödinger equation can be decoupled into an electronic and nuclear equation. The electronic Schrödinger equation is solved and then the electronic energy is added to the internuclear repulsion inorder to obtain the total internal energy of a molecule. An outcome of the Born-Oppenheimer approximation is that a molecule has a shape[12]. Considering the complete molecular Hamiltonian,

$$H = T_e + V_{\text{ee}} + T_N + V_{\text{NN}} + V_{\text{eN}} \tag{2.3.7}$$

which includes kinetic energy of electrons (T_e), electron-electron repulsion Coulomb potential (V_{ee}), kinetic energy of nuclei (T_N), nuclear-nuclear repulsion Coulomb potential (V_{NN}), electron-nuclear attractive Coulomb potential (V_{eN}). The Schrödinger equation is,

$$\hat{H}\Psi(r, R) = E\Psi(r, R) \tag{2.3.8}$$

Applying Born-Oppenheimer approximation,wave function Ψ can be separated into a product of electronic and nuclear parts;

$$\Psi(r, R) = \psi(r, R)\chi(R) \tag{2.3.9}$$

where ψ is a wavefunction of electronic part of the Schrödinger equation and χ is a wavefuntion associated with nuclear motion. While solving electronic Schrödinger equation, the nuclei kinetic energy can be neglected[8];

$$(T_e + V_{\text{NN}} + V_{\text{eN}} + V_{\text{ee}})\psi = E_{\text{el}}(R)\psi \tag{2.3.10}$$

where E_{el} is the electronic energy as a function of nuclear coordinates R. Inserting (2.2.14) and (2.2.13) into (2.2.12), we obtain

$$(T_N + E_{\text{el}})\psi\chi = E_{\text{tot}}\psi\chi \tag{2.3.11}$$

According to Born-Oppenheimer approximation, ψ can be integrated out from both sides of (2.2.15), giving nuclear Schrödinger equation.

$$(T_N + V)\chi = E_{\text{tot}}\chi \tag{2.3.12}$$

in which $V = V_{\text{NN}} + E_{\text{el}}$ is the electronic potential surface energy[8].

The nuclei view electrons as a smear cloud of negative charge which binds them in fixed relative postions. The nuclear coordinates are the permanent geometric parameters of a molecule due to the rapid motion of the electrons. Since the nuclei are massive, they are relatively stationary unlike the electrons, which imparts a definite shape to a molecule. If the masses of the nuclei and electrons could be made equal, the distinction in lethargy would be lost, thereby the molecular geometry would dissolve. Thus, Born-Oppenheimer approximation is a cornerstone of computational chemistry as it makes the concept of molecular shape(geometry) meaningful and simplifies the application of Schrödinger equation to molecules by letting us to focus on electronic energy and then add the nuclear repulsion energy[12].

3.3 Potential Energy Surface (PES)

The Potential Energy Surface is an outcome of the application of Born-Oppenheimer approximation to the solution of the Schrödinger equation. The Born-Oppenheimer principle serves as a prerequisite for the concept of a potential energy surface. is a mathematical or graphical relationship between the energy and geometry of a molecule. Carrying out the calculations of the electronic energy for different sets of nuclear coordinates yields the PES. A nonlinear system consisting of N atoms has 3N-6 independent coordinates (degrees of freedom) which exhibits the potential energy surface[19].

A full-dimensional PES can be calculated using computational chemistry calculations. The local minima corresponds to stable molecule. The minimum energy pathway which connects minimas describes reaction mechanism. The maxima which has highest point energy along reaction mechanism pathway corresponds to transition state and using the transition state theory, one can calculate the rate constant of the reaction. However, all parameters of a reaction a mechanism cannot be obtained only by studying the stationary points of the PES, for example, resonance and tunneling effects. Such parameters can be studied by applying molecular quantum dynamics. Moreover, generating a full dimensional PES in practice is very difficult except for small systems[8].

4 Electronic Structure Theory

Electronic structure theory computes solutions to the electronic Schrödinger equation. Potential Energy Surface (PES) can be determined by two types of methods: electron ave function based methods and electron density based methods. This section describes principles which are common to methods based on electron wave function and electron density.

4.1 Variational Method

Inorder to obtain approximate solution to the Schrödinger equation, the lowest energy eigen state or ground state has to be determined. According to the variational principle, the energy of an approximate wave function is always too high. Hence energy is one measure of quality of a wave function, the lower the energy, the better the wave function[20]. The variational method comprises of a trial wave function which has higher expectation value of energy than the exact energy.

$$E_{\text{trial}} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_o \qquad (2.4.13)$$

where E_o is the exact ground state energy value and ψ is normalised. The function ψ is called trial variation function and the integral is called variational integral. The variational method allows to determine trial wave function with lowest possible energy which is closest to the correct solution[8].

4.2 Basis Set

A basis set is a set of functions, called basis functions χ_j, which represent electronic wave function from which molecular orbitals of trial wave function can be constructed.

$$\phi_i = \sum_{\mathrm{j}}^{M} C_{\mathrm{i,j}} \chi_j \qquad (2.4.14)$$

where M is number of basis function. Increment in number of basis function gives molecular orbitals of trial wave function closer to the exact solution. But, use of large number of basis functions enhances cost of optimization[8]. The unknown molecular orbitals can be approximated by expanding them in terms of known functions, that is, a basis set. The major types of basis functions for molecular quantum mechanical calculations are Slater Type Orbitals (STOs) and Gaussian Type Orbitals (GTOs). In comaprison to STOs, GTOs are computationally easier and more efficient. Using linear combinations of multiple GTOs a good accuracy can be attained[21].

5 Electron Wave Function Based Method

5.1 Hartree-Fock Approximation

Hartree-Fock method is considered as starting point in ab initio calculation[22]. It provides an approximate solution to the electronic Schrödinger equation[8]. The primary approximation is the central field approximation, according to which the Coulombic electron-electron repulsion is accounted by integrating the repulsion term. This provides average effect of repulsion. It is a variational calculation i.e. the approximate energies calculated are equal to or greater than exact energy. In this method, the energies are calculated in units called Hartrees, where 1 Hartree =27.2116 eV or 627.509 kcal/mol[14].

This method introduces independent-particle models, where motion of one electron is considered to be independent of the dynamics of all other electrons[23]. It separates the many-electron Schrödinger equation into many elemenatry one-electron equations, which yield single-electron wavefunctions called orbitals and energies called orbital energies[14]. The Pauli principle describes a wave function as antisymmetric, in order to assure this the total electronic wave function is expressed by the Slater determinant instead of a single product of molecular orbitals. Equation 2.5.15 shows the general Slater determinant for a system with N occupied spin orbitals, ψ is the total wavefunction and χ represent spin-orbitals[8].

$$\psi(x_1, x_2, ...x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \dots & \chi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \chi_1(x_N) & \chi_2(x_N) & \dots & \chi_N(x_N) \end{vmatrix} \tag{2.5.15}$$

In this model, each electron is described by orbital and total wave function is expressed as a product of orbitals. By reason of electrons being identical fermions, by arranging the orbitals in Slater determinant all antisymmetric wavefunctions can be achieved. Hartree-Fock model is regarded as bifurcation point, where either further approximations can be used to form semi-empirical methods or it can be upgraded by adding additional determinants to construct models inorder to obtain exact solution of electronic Schrödinger equation[23].

The n-electron Schrödinger equation is mathematically converted to one-electron Hartree-Fock equation by reducing the total energy of Schrödinger equation.

$$f_i \chi_i(x_i) = \varepsilon_i \chi_i(x_i) \tag{2.5.16}$$

where f_i represents Fock operator, ε_i is an eigen value value denoting orbital energy. Fock operator is one-electron operator for a spin orbital and is defined as

$$f_i = h_i + \sum_{j}^{n} \{J_j - K_j\} \tag{2.5.17}$$

where h_i denotes kinetic energy and Coulomb potential energy between electrons and nucleus; J_j and K_j are Coulomb operator and exchange operator respectively[8].

Nevertheless, large deviations are seen from the experimental results due to negligence of electron correlation. This is the drawback of HF method. Electron correlation can be split into non-dynamical (static) correlation and dynamical correlation. Post-Hartree-Fock methods have been designed to include electron correlation to the multi-electron wave function. The multi-configurational wave function methods describe static correlation, while, dynamical correlation is described by Configuration Interaction (CI), Coupled-Cluster (CC), Møller-Plesset perturbation theory (MP) etc[8].

5.1.1 Self-consistent field (SCF)

The HF equations are nonlinear and have to be solved iteratively by using the self-consistent field (SCF) procedure. It involves selection of an approximate Hamiltonian used to solve the Schrödinger equation to obtain a more accurate set of orbitals. The Schrödinger equation is solved again with theses until the results converge[8]. The lower boundary for the ground state energy is obtained by using the variational principle. But the energy obtained will be higher or equal to the exact energy. The energy is calculated by dividing the expectation value of the Hamiltonian operator by the average wave function, see equation 2.5.18.

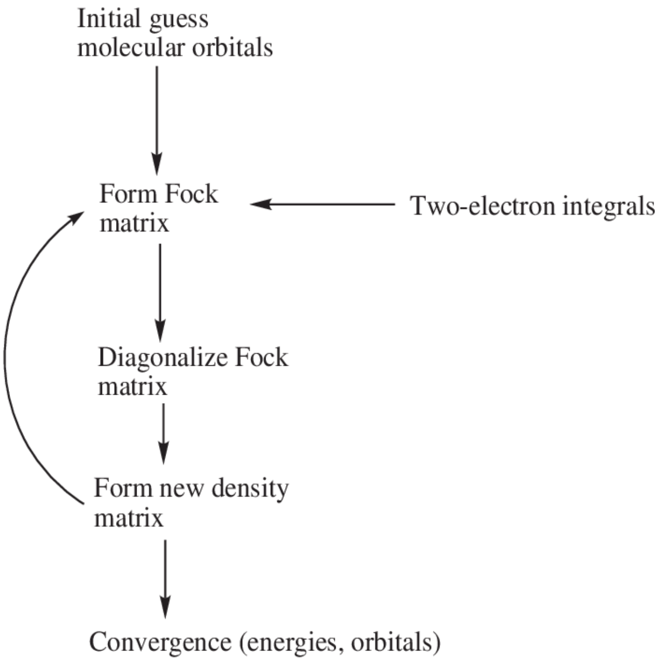

Figure 2.2: Illustration of SCF procedure

$$E_e = \frac{<\psi|H_e|\psi>}{<\psi|\psi|>} \tag{2.5.18}$$

The SCF procedure is schematically described in figure 2.2. The Fock-matrix comprises of Fock-equations in a matrix notation. These equations are derived with basis set approximation by product of HF equations with specific basis function. By diagonalizing the Fock-matrix, the molecular orbitals (MO) coefficients are determined. Guessing the coefficients, form the matrix and diagonalizing it, new coefficients are obtained which are used to construct a new matrix until the coefficients given are close enough to those used up to a predetermined accuracy[21].

5.2 Configuration Interaction (CI)

Configuration interaction (CI) is a variational method used to solve the non-relativistic Schrödinger equation within the Born Oppenheimer approximation. It includes electron correlation in molecular calculations. The CI wave function is described as a sum of various slater determinants in which the coefficients of the slater determinant summation are variationally optimized as:

$$\psi = \sum_i c_i D_i \tag{2.5.19}$$

where the determinants D_i are attained by the excitation of electrons from occupied orbitals of the HF ground state to unoccupied orbitals. The determinants are classified on the basis of the number of excited electrons. For example, the determinants in which one electron is excited are referred as single excitations. Similarly, if only single and double excitations are included it is called singles $-$ doubles CI (CISD). The drawback of CI is that it is not size-consistent. So as to correct the size-consistency errors, CI is extended to develop Quadratic configuration interaction (QCI). Moreover, full CI (FCI) is a CI expansion in which all possible excitations are included and it gives the accurate answer within the chosen basis, but the cost of the CPU time is not feasible[8].

5.3 Coupled-Cluster (CC)

Coupled-cluster (CC) is a technique used to describe electron correlation in many-body systems. It utilizes a wave function obtained from the HF wave function (ψ_0) to construct multi electron wave function that employs the exponential cluster operator for electron correlation.

$$\psi_{CC} = e^{\hat{T}} \psi_0 \tag{2.5.20}$$

The exponential of $\hat{T}$ is expressed as:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \cdots = \sum_{k=0}^{\infty} \frac{1}{k!}\hat{T}^k \tag{2.5.21}$$

The coupled cluster singles and doubles (CCSD), is one of the most widely used version of coupled-cluster. It duplicates the allowed curvature of potential energy in regard to the bond length i.e. Morse's potential curve. However, the energy obtained is too high and therefore, to lower the energy and obtain an improved potential energy curve, higher than doubly excited determinants have to be considered. Additionally, the effects of triple excitations are included using perturbative approach giving the CCSD(T) method[8].

5.4 Møller–Plesset (MP) perturbation theory

Electron correlation can be included by addition of interelectronic Coulomb interactions as a perturbation from the Hartree Fock wave function. This is called Møller–Plesset (MP) perturbation theory. It is extensively used for approximating the correlation energy of molecules[8]. It is based on the Rayleigh-Schrödinger Perturbation Theory(RSPT) in which the wave function is expanded and a Taylor series expresses the corresponding energies as a perturbation parameter. In comparison of HF wave function with perturbation theory, HF becomes a first-order perturbation. With the addition of minimal amount of correlation, second-order MP2, third-order (MP3) and fourth-order (MP4) methods are obtained. MP4 calculation has accuracy analogous to the accuracy of a CISD calculation. Nevertheless, MP5 and higher calculations are infrequent due to the high computational cost. Møller–Plesset (MP) perturbation theory is advantageous as it is size extensive. Its calculations are not variational and can yield total energies below the exact total energy[14].

6 Electron Density Methods

6.1 Density Functional Theory

The Density Functional Theory was first put forth by Walter Kohn and Pierre Hohenberg in the configuration of the two Hohenberg–Kohn theorems. It is one of the most used techniques to calculate molecular structures as it requires less computational effort and computer time[24]. For systems comprising of small number of electrons and nuclei, precise solution for Schrödinger equation can be obtained by using different wavefunction methods. But for larger systems of heterogeneous catalysis, it becomes quite challenging. Hohenberg and Kohn provided the basis of DFT, which decreased the difficulty of N interacting electrons with 3N degrees of freedom to only three degrees of freedom. They proclaimed that there is a one-to-one correspondence between ground state energy and the ground state electron density. Hence the total energy can be expressed as a function of electron density ρ,

$$E[\rho] =< \Psi[\rho]|H|\Psi[\rho] > \tag{2.6.22}$$

However, equation 2.6.22 does not say anything about the form of the functional dependence of the energy on density; it only tells that such a functional exists. This is known as the Universal Hohenberg-Kohn functional. The second Hohenberg-Kohn theorem defines an energy functional for the system and shows that the correct ground state electron density minimizes this energy functional[25].

The objective of DFT is to design functionals with sufficient accuracy which connects the electron density with the energy. A general expression for the DFT energy is expressed as equation 2.6.23. The Kohn-Sham (KS) method is employed to solve for the energy.

$$E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J_\rho + E_{XC}[\rho] \tag{2.6.23}$$

$T_S[\rho]$ is the kinetic energy, $E_{ne}[\rho]$ is attraction between nuclei and electrons, $J[\rho]$ is the coulomb part in the electron-electron repulsion and $E_{XC}[\rho]$ is the exchange-correlation[21]. KS-DFT operates by combination of SCF, which treats kinetic energy, with an explicit functional for density; hence, kinetic energy is evaluated in terms of orbitals called KS-orbitals. Electron density is calculated by using Slater determinant and in turn, T_S and electrostatic energies are obtained, see figure 2.3[21].

The foundation of Density Functional Theory is determination of ground state

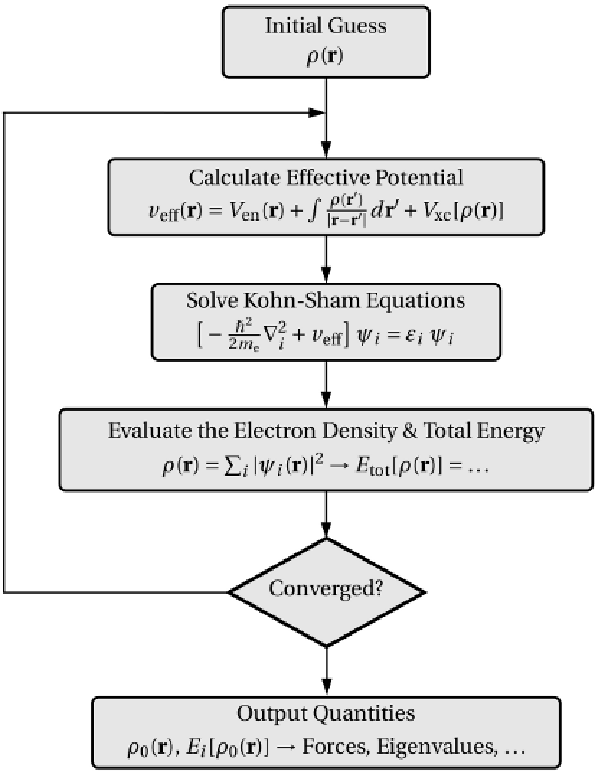

Figure 2.3: Illustration of iterate method to find energy minima in DFT

electronic energy with the utilisation of electron density ρ(x,y,z). The electronic density exhibits probability of finding an electron in a volume element dxdydz. In a scatterplot of electron density in a molecule, the variation of ρ with position can be specified by the density of points. The electron density function is not only the basis of DFT, but of a entire series of methods which study atoms and molecules. In contrast to the wave function, electron density function is measurable by X-ray diffraction or electron diffraction. Furthermore, electron density is a function of position only i.e. of just three variables (x,y,z); while the wave function of an n-electron molecule is a function of 4n variables[12].

In DFT method, electron density is expressed as a linear combination of basis functions from which a determinant of orbitals is formed inorder to compute the energy. Thus, a density functional is used for obtaining energy for electron density[14]. In spite of the fact that each different density gives a different ground state energy, the functional connecting electron density and energy is unknown. A functional is a function of a function. Electron density is a function, while the energy dependent on electron density is a functional[23]. The primacy of electron density is that the integrals for Coulomb repulsion are required to be performed only over the electron density[14].

The simplest model is the local density approximation, which is based on assumption that the electron density changes slowly, allowing calculation of exchange-correlation energy possible. DFT is conceptually and computationally parallel to Hartree-Fock theory, however provides better results and therefore has become a very famous technique. Nevertheless, the main drawback of DFT is the incapability to efficiently improve the results, which has given rise to bafflement of different functionals with insignificantly different performances for various properties[23].

In DFT method, the energy of the molecule is a function of the electron density, $E(\rho)$, which in turn is a function of position, $\rho(r)$. The equation for electron density is defined as:

$$\rho(r) = \sum_m |\psi_m(r)|^2 \tag{2.6.24}$$

ψ_m is calculated from the Kohn-Sham (KS) equations. The Kohn-Sham equations are defined as:

$$[\hat{h}(l) + \int \frac{\rho(2)}{r_{12}} d\tau_2 + V_{XC}(1)]\psi_m(1) = \varepsilon_m \psi_m(1) \tag{2.6.25}$$

The DFT methods face difficulty in construction of the exchange-correlation potential V_{XC}. There are various density functional theory functionals to choose among[24].

A functional produces a number from a function that depends on variables and are denoted with brackets, F[x]. Hybrid DFT functionals are constructed by hybridizing E_{XC} orbital-based HF exchange energy functional[14]. The most frequently used hybrid functional is B3LYP which was developed from the GGA functional BLYP. B3 is Becke's three parameter exchange correlation functional. It employs 3 parameters to utilize the exact Hartree-Fock exchange correlation and LYP, i.e. Lee, Yang and Parr correlation functional[18]. It includes the exact exchange and gives more accurate energies. It is relatively fast and can handle rather large systems[21]. The exchange correlation functional of B3LYP is expressed as:

$$E_{XC}^{B3LYP} = E_{XC}^{LDA} + \alpha_0(E_X^{HF} - E_X^{LDA}) + \alpha_X(E_X^{GGA} - E_X^{LDA}) + \alpha_C(E_C^{GGA} - E_C^{LDA}) \tag{2.6.26}$$

where α_0, α_X, α_C are universal parameters appropriate to experimental data with values of 0.20, 0.72 and 0.81, respectively. E_X^{GGA} and E_C^{GGA} are generalized gradient approximations; E_C^{LDA} is local-density approximation to the correlation functional[8].

7 Gaussian Theory

The Gaussian methods are distinctive types of computations. Ab initio methods showed systematic errors in predicting the energies of the ground states, which led to the development of Gaussian methods. They use a correction equation that uses the energies from various ab initio calculations to extrapolate to a very-high-accuracy result. However, all the calculations that go into this extrapolation are of ab initio methods. The extrapolation equation is an empirically defined equation parameterized to reproduce results from a test set of molecules as accurately as possible. Hence, these methods show the same strengths and weaknesses as semi empirical methods[14].

8 Transition State Theory

The transition state theory is also called theory of absolute reaction rates and the theory of activated state. It is an important redefined version of crude collision theory, which treats reactants as rigid spheres and doesn't consider their structural aspects. The theory explains chemical reaction rates assuming quasi-equilibrium,i.e. infintesimal deviation from equilibrium, between reacting molecules and transition state complexes. The transition state, i.e. activated state decomposes to form the products. The reaction rate becomes equal to decomposition rate of activated complex. The fundamental assumption of transition state theory is the existence of activated state which is formed by activation of reactants. The collisions between reactants form an unstable, high energy activated state called transition state which then decomposes to form the product of reaction. The activated state is a saddle point with positive curvature in all degrees of freedom[26].

The kinetic energy of colliding molecules, with sufficient energy and proper orientations, is tarnsformed into potential energy and the activated complex is characterised by positive molar Gibbs energy. The difference between the transition state and the ground state of reactants yields the standard Gibbs energy of activation. The transition state formed is highly energetic and unstable intermediate having temporary existence and decomposes to form products. The rate of decomposition of transition state gives the rate of reaction.

Transition state theory presumes that a chemical reaction progresses in two steps: i) formation of activated complex ii) decomposition of activated complex into the products. Figure 2.4 shows Potential energy profile for exothermic (a), endothermic (b), multistep process (c) and catalyzed reaction (d). Catalysts provide an alternate pathway for a reaction with lower activation energy and

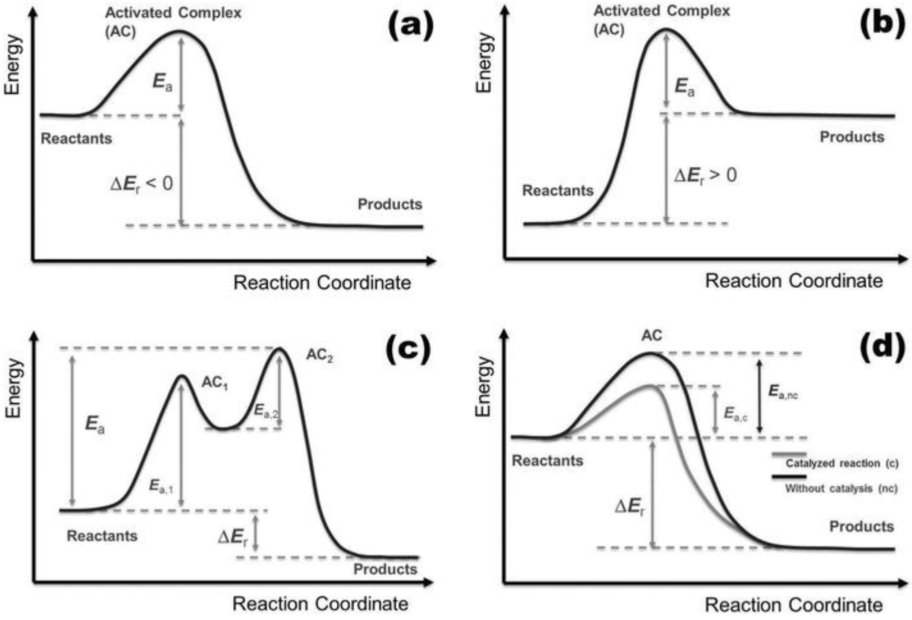

Figure 2.4: Potential energy diagram

hence the rate of reaction increases[26].

Although transition state theory gives a conceptual base to understand the rate of elementary reaction on molecular scale, contrarily, it fails if applied to each elementary steps of a multistep reaction. It also fails for some reactions at high temperatures because of complex motion of molecules or at very low temperatures because of quantum tunneling[26].

Transition state theory is constructed on various mathematical assumptions. The theory assumes that Maxwell-Boltzmann statistics can predict number of molecular collisions which have energy greater than or equal to the activation energy. This is called quasi-equilibrium because it is similar to assuming that the molecules at the transition structure are in equilibrium with the reactant molecules, even though molecules do not stay at the transition structure long enough to achieve equilibrium. Moreover, it also assumes that the molecules which reach the transition point react irreversibly[14].

The state of reaction is given by the rate of decomposition of activated complex. The theoretical computation of a rate constant using transition state theory generally involves the location of all necessary stationary points, one transition state structure and one or two minima and evaluates their energies and their partition functions under the rigid-rotor-harmonic-oscillator approximation. Experimental scrutiny alternatively measures rate constants to derive quantities such as free energy of activation, enthalpy and entropy. Analysis of experimental data involves carrying out rate constant measurements at a series of sequential temperatures and plotting an Erying plot of $ln(\frac{k}{T})$ against $(\frac{1}{T})$ [26].

$$k = \frac{k_B T}{h} e^{-\frac{\Delta H}{RT}} e^{-\frac{\Delta S}{R}} \tag{2.8.27}$$

Where ΔH^o is standard change in enthalpy, ΔS^o is standard entropy change, k_B is Boltzmann constant, h is Planck's constant, T is temperature in Kelvin and R is gas constant.

The linear form of the Eyring Equation is given by,

$$ln\frac{k}{T} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + ln\frac{k_B}{h} \tag{2.8.28}$$

Which indicates that the slope of such a plot should be $\frac{-\Delta H}{R}$ and intercept is a function of $\frac{\Delta S}{R}$ using this quantities, the free energy activation can be easily calculated for any temperature within the range of the data points and compared to a theoretical calculation of such a quantity. And alternatively approach is to plot ln(k) vs $\frac{1}{T}$, a procedure empirically derived by Arrhenius expression,

$$k = Ae^{\frac{-Ea}{RT}} \tag{2.8.29}$$

Where A is pre-exponential factor and E_a is the Arrhenius activation energy. A plot of ln(k) vs $\frac{1}{T}$ will have slope of $\frac{Ea}{R}$ and intercept ln A. The relation between Arrhenius quantities and thermodynamic quantities can be given as

$$Ea = \Delta H^o + RT \tag{2.8.30}$$

and

$$A = \frac{k_B T}{h} e^{(1+\frac{\Delta S^o}{R})} \tag{2.8.31}$$

These two conventions indicate that the term 'activation energy' is used without qualification and for accurate comparisons it has to be established whether this term refers to Arrhenius activation energy, or a transition state theory activation free energy or a difference in stationary point potential energies [18].

3

Results and Discussion

This chapter explains the methodology and results obtained in this dissertation. The computational quantum chemical calculations were performed using Gaussian 09 program. It was used to carry out geometry optimizations, calculate molecular energies, study vibrations among many of other things. Firstly, the structures of required molecules were created using Avogadro software. The geometries were optimized in Gaussian-09 with density functional B3LYP and 6-31G basis-set as implemented in the Gaussian 09 program. Solvent effects were also included in input file using acetonitrile as solvent. After the completion of calculations, they were saved in output file which were read using a text program. Information about the geometry, energy of the molecules as well as vibration frequencies and CPU time was obtained from the calculations. Gaussian provided a useful scan function. By scanning a coordinate, changes in bond length or angle were made in smaller steps and the program calculated the energy optimized structures at each point.

Some transition state geometries were successfully estimated using the distance estimates, while, the geometries of the remaining transition states were calculated using QST3 method, in which, calculations were run with the structure of the reactants in one window and the structure of the products in another window. Providing three molecule specifications: the reactants, the products, and an initial structure, the QST3 calculations were run. The program then calculated the transition state's geometry and the result was obtained in a new window. Since it is next to impossible to analyze the transition state experimentally, there were no values to compare the theoretical calculations of transition states. Moreover, it was not possible to perform the TS calculations with the B3LYP method as Gaussian 09 only gave error messages. Gaussian 09 calculated all vibrations for the transition state.

The resultant vibration frequencies were studied and it was observed that

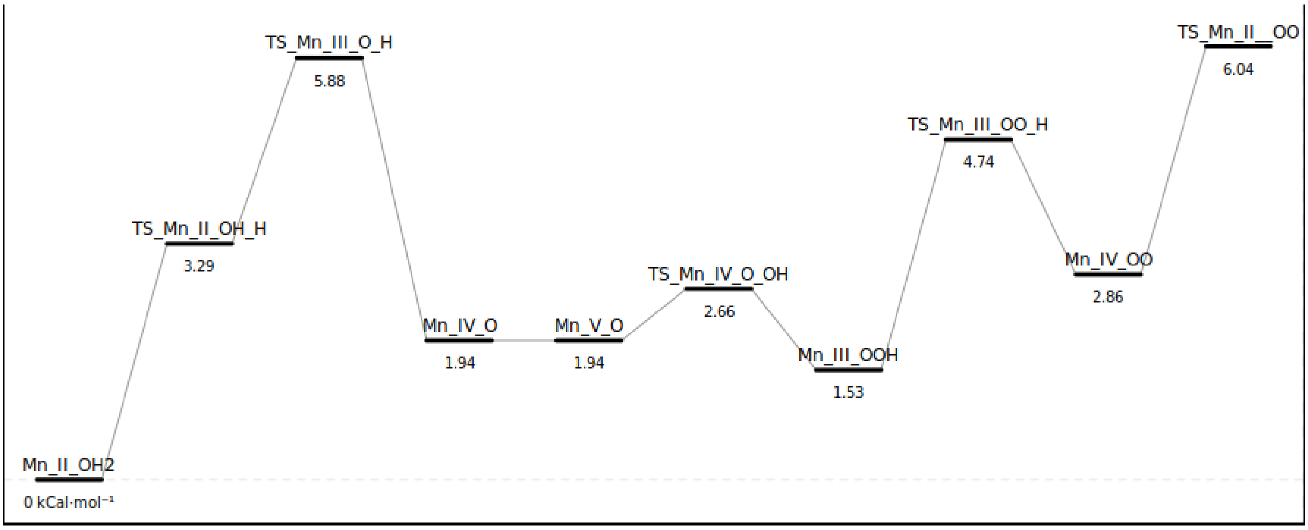

Figure 3.1: Energy diagram for water oxidation catalyzed by Mn complex

smaller bonds have high frequency, while relatively long bonds showed low vibration frequencies. Furthermore, frequencies were computed to verify the nature of all the stationary points and also to obtain Gibbs free energy corrections at 298.15 K. On the basis of the optimized geometries, the final and the solvation energies in water were calculated as single-point corrections using the continuum solvation model. Singlet-point calculations using B3LYP were also carried out to evaluate redox potentials. To evaluate sensitivity of the redox potentials from computations, the Born-Haber Cycle was employed. To calculate the redox potentials for all oxidation steps, the experimental absolute redox potential of the standard hydrogen electrode (SHE, 4.281 V) was used as a reference.

Investigation begins from the hexa-coordinated Mn^{II} complex **1** (figure 1.1), the ligand framework of which is composed of ($L=N_3Py_2$), three amines, two pyridines and one aqua ligand. In order to identify the most stable structure at the working pH (pH= 5.2, 7.0, 8.0), various protonation states need to be considered. Complex **1** as shown in figure 3.3, has one water molecule and is a high-spin sextet with Mn in +2 oxidation state. The oxidation of **1** is associated with the release of two protons which occurs due to high pH, as proposed in mechanism in figure 1.2. At normal pH of 7 this step of oxidation would be quite costly.

The quintet transition state TS-Mn-II-OH-H complex **2**, shown in figure 3.4, is generated which is 3.29 kcal/mol higher. The redox potential for this oxidation step was calculated to be 0.09 V and this step is thus endergonic with an applied potential of 1.23 V. Next, a proton-coupled electron transfer (PCET) oxidation leads to the formation of species TS-Mn-II-OH complex **3**, figure 3.5, which is

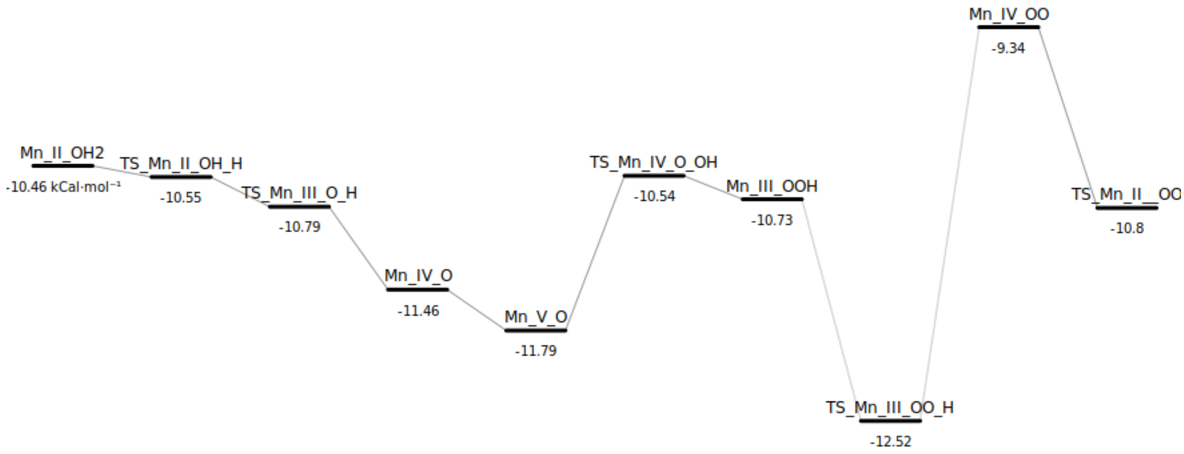

Figure 3.2: Redox potential diagram for water oxidation catalyzed by Mn complex

5.88 kcal/mol higher and is associated with a redox potential of 0.24 V. This oxidation process is endergonic by 2.59 kcal/mol. Species **3** is a high spin anti ferromagnetically coupled to an oxyl radical complex which also involves some $Mn^{IV} = O$ character.

The subsequent proton coupled electron transfer leads to the generation of a quartet d^3 system **4**, as shown in figure 3.6, which is 1.94 kcal/mol higher. The redox potential for this oxidation step was calculated to be 0.67 V. Also, it is exergonic by 3.94 kcal/mol. This step is difficult to determine whether the oxidation is a PCET process or a one electron process. Further, there is one electron transfer which forms a triplet Mn^{V} complex **5** $[\mathrm{LMn}^{\mathrm{V}} =\mathrm{O}]^{3+}$, figure 3.7, which is also 1.94 kcal/mol higher and has a redox potential of 0.33 V.

The O-O bond formation is initiated by the formal Mn^{V} state. A water molecule initiates a nucleophilic attack on the $\mathrm{Mn}^{V} = O$ moieties. The transition state TS-Mn-IV-O-OH complex **6** for the oxo-oxo coupling at the Mn^{V} state is shown in figure 3.8. It is only 2.66 kcal/mol higher which implies that it is endergonic by 0.72 kcal/mol relative to **5**. The transition state complex **6** is formed with a gain in potential of 1.25 V. In this transition state the two oxygen atoms have opposite spins, which is required for an efficient O-O bond formation. The oxygen atom in complex **5** functions as a general base to abstract a proton from the water molecule during the attack.

Further, upon addition of water molecule, there is a proton loss leading to formation of quintet complex **7** $[\mathrm{LMn}^{\mathrm{III}}\text{ -OOH}]^{2+}$. This complex **7**, shown in figure 3.9, is quite stable, has energy of 1.53 kcal/mol higher and is exergonic by 1.13 kcal/mol. A subsequent fall in potential of 0.19 V is seen in formation of intermediate complex **7**. The electronic structure of complex **7** can be best characterized as Mn^{III}-peroxo.

There is oxidation from d^4 to d^3 system by loss of a proton and an electron to form complex **9** $[LMn^{IV}\text{-}OO]^{2+}$, figure 3.10, which is 2.86 kcal/mol higher and is formed with a gain in potential of 3.18 V relative to complex **8**. It is exergonic to its corresponding transition state TS-Mn-III-OO-H complex **8**, shown in figure 3.11, by 1.88 kcal/mol which is 4.74 kcal/mol higher. The redox potenatial difference between species **7** and **8** is 1.79 V, which is slightly higher than the applied potential (1.23 V), suggesting that this oxidation process is endergonic by 3.21 kcal/mol. There is a large potential gap between complex **8** and complex **9** of 3.18 V.

Finally, upon addition of water molecule to complex **9**, the Mn-oxo bond breaks to evolve O_2 molecule and complex **1** gets regenerated with attachment of aqua ligand with the formation of transition state TS-Mn-II-OO complex **10** which has energy barrier of 3.18 kcal/mol. Complex **9** loses a oxygen molecule with a downfall in potential of 1.46 V and recombines with a water molecule to form back complex **1**.

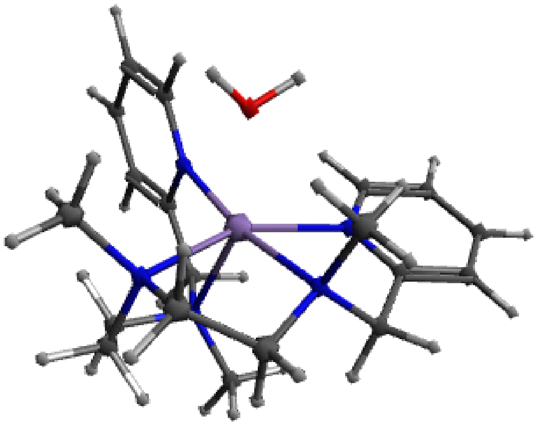

Figure (3.3) $Mn^{II}-OH_2$

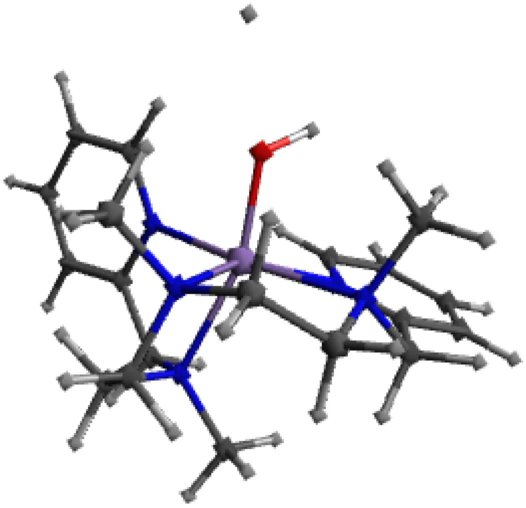

Figure (3.4) TS-$Mn^{II}-OH-H$

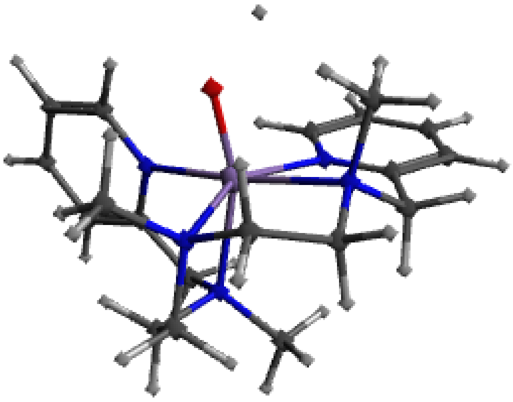

Figure (3.5) TS-Mn$^{III}-O-H$

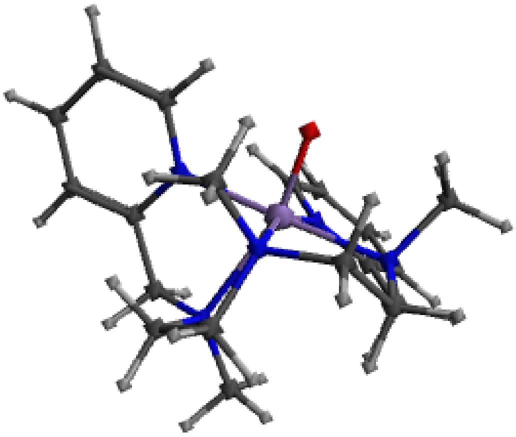

Figure (3.6) Mn$^{IV}-O$

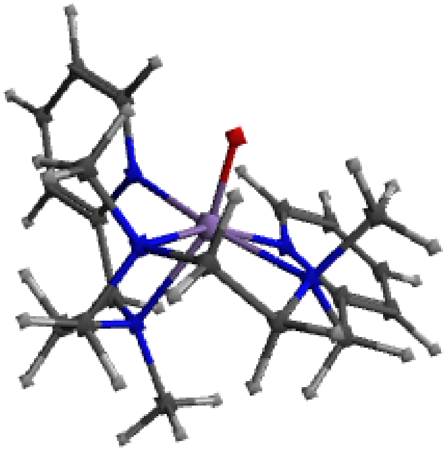

Figure (3.7) Mn$^{V}-O$

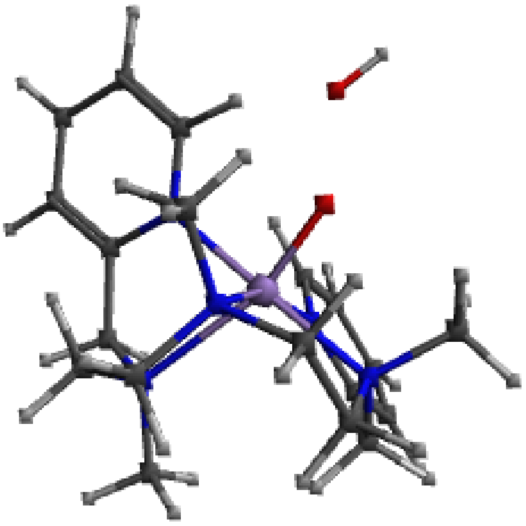

Figure (3.8) TS-Mn$^{IV}-O-OH$

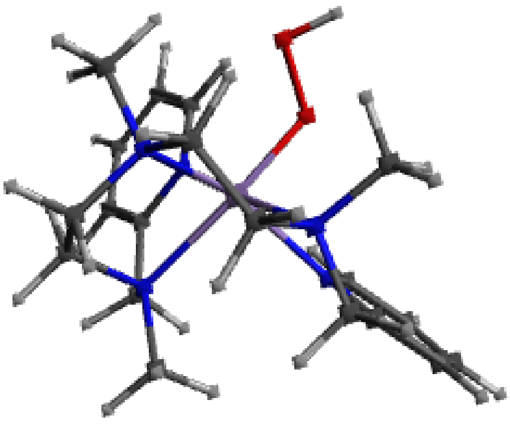

Figure (3.9) Mn$^{III}-OOH$

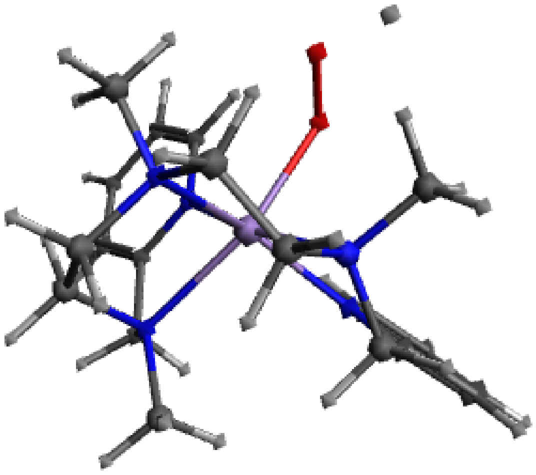

Figure (3.10) TS-Mn$^{III}-OO-H$

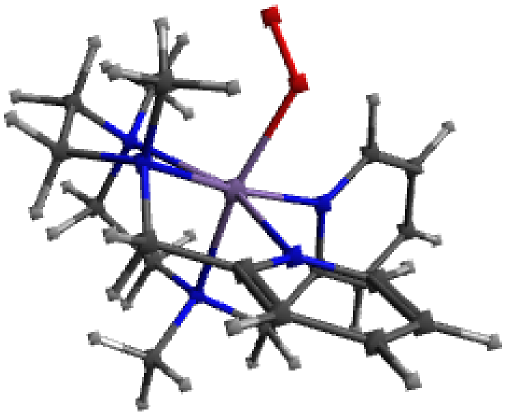

Figure (3.11) Mn$^{IV}-OO$

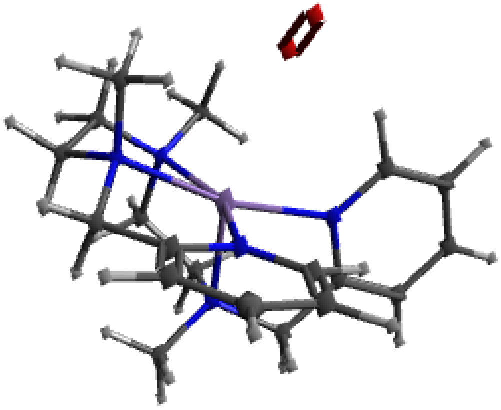

Figure (3.12) TS-Mn$^{II}-OO$

4

Conclusion

In this dissertation, the water oxidation mechanism of $[Mn(N_3\ Py_2\ )H_2\ O]^{2+}$ has been investigated using density functional calculations. Various transition states, reaction intermediates, redox potentials were calculated. The whole catalytic cycle is summarized in figure 1.2 and the corresponding energy diagram is shown in figure 3.1. Three sequential oxidations of $[LMn^{II}(H_2O)]$ result in generation of a formal species $[LMn^{V}{=}O]$, from which critical O-O bond formation proceeds via water attack which has very high energy barrier. Finally, oxygen evolution occurs from $[LMn^{IV}\text{-}OO]$, followed by water binding and de-protonation to regenerate $[LMn^{II}(H_2O)]$ for the next catalytic cycle. Furthermore, redox potentials and energy barriers were also studied for each step of the proposed mechanism of water oxidation.

5

Supporting Information

Sample input file (TS1.gjf) for transition state calculations

```
%NProcShared=2
%chk=TS_Mn_II_OH2.chk
#P Becke3LYP/6-31G(d) opt=(ts,calcfc,noeigen) iop(1/7=30) freq

TS_Mn_II_OH2

2 6
Mn        -0.05909      -0.32250      -0.32208
N          1.92559       0.67764      -0.50267
N          0.77002      -0.37517       1.79286
N         -2.23895      -1.10475      -0.37666
N         -1.31532       1.46260      -0.07263
N          0.30018      -2.53509      -0.17110
O         -0.02412      -0.23425      -2.56117
H          0.29923      -0.87806      -3.24225
H         -1.31820       1.45874      -4.06438
C         -1.73496       3.83596      -0.11524
H         -1.35984       4.83767      -0.27790
C         -3.06761       3.61326       0.24255
H         -3.75181       4.44425       0.36110
C         -2.87952      -1.06565      -1.74240
H         -2.28758      -1.64632      -2.44830
H         -2.92698      -0.02888      -2.08195
H         -3.89788      -1.47209      -1.69971
C         -3.01364      -0.19284       0.53455
```

H	-2.76800	-0.45650	1.56966
H	-4.09621	-0.31613	0.40454
C	2.51630	1.01157	0.67690
C	-2.61222	1.24964	0.28031
C	-0.89202	2.74145	-0.26486
H	0.14774	2.86749	-0.54246
C	-0.99382	-3.26336	-0.47513
H	-1.09585	-3.31155	-1.56250
C	1.68766	0.81256	1.92655
H	2.33747	0.71030	2.80527
H	1.04983	1.69209	2.07932
C	-2.19278	-2.52260	0.13374
H	-3.11938	-3.06084	-0.10518
H	-2.10457	-2.48652	1.22318
C	2.61633	0.89542	-1.65541
C	3.79973	1.54947	0.73079
H	4.24292	1.79294	1.68831
C	-3.50899	2.30282	0.43875
H	-4.53746	2.09976	0.71031
C	1.57452	-1.65715	1.80643
H	1.90963	-1.88668	2.82642
H	2.46017	-1.50059	1.18563
C	0.73894	-2.81553	1.25587
H	1.31668	-3.74736	1.29368
H	-0.15288	-2.95675	1.86879
C	-0.19652	-0.34916	2.95040
H	-0.86365	-1.21064	2.89676
H	-0.78867	0.56733	2.89515
H	0.33561	-0.37747	3.90995
C	4.49921	1.77089	-0.45681
H	5.49762	2.18964	-0.43453
C	3.89359	1.43958	-1.67191
H	4.40476	1.59765	-2.61233
H	2.10214	0.62093	-2.56327
C	1.38369	-3.00560	-1.11337
H	2.29864	-2.43998	-0.92430
H	1.06455	-2.83233	-2.14419
H	1.58570	-4.07578	-0.98453

```
H         -0.95719       -4.29383       -0.09890
```

Cartesian coordinates of optimized structures:

1. Mn_II_OH2

```
57
E_tot= -2242.215262 Max-Force= 0.000000 YES
Mn        -0.050201   -0.274318   -0.340025
 N         1.956109    0.758546   -0.505621
 N         0.891310   -0.469111    1.799192
 N        -2.276402   -1.097851   -0.352555
 N        -1.362493    1.503934   -0.006765
 N         0.288141   -2.577855   -0.228442
 O        -0.080758   -0.250414   -2.695288
 H         0.447426   -0.749689   -3.340017
 H        -0.715696    0.264835   -3.220223
 C        -1.856939    3.859092   -0.020986
 H        -1.507074    4.873713   -0.177759
 C        -3.177145    3.592982    0.343178
 H        -3.888597    4.402146    0.476999
 C        -2.954411   -1.042858   -1.671683
 H        -2.408516   -1.636040   -2.405985
 H        -2.999435   -0.007428   -2.019476
 H        -3.981381   -1.426782   -1.601133
 C        -2.993565   -0.209405    0.593147
 H        -2.693180   -0.477132    1.613055
 H        -4.081437   -0.352548    0.537639
 C         2.606561    0.956910    0.664589
 C        -2.643407    1.246900    0.347725
 C        -0.986899    2.787395   -0.187680
 H         0.048450    2.947434   -0.474707
 C        -1.018956   -3.244742   -0.504225
 H        -1.144887   -3.286754   -1.589758
 C         1.842189    0.660945    1.936432
 H         2.542428    0.485640    2.765331
 H         1.257086    1.549632    2.204739
 C        -2.197005   -2.502042    0.129733
```

H	-3.125431	-3.049887	-0.084008
H	-2.093936	-2.484059	1.218859
C	2.583885	1.109161	-1.649369
C	3.897139	1.482983	0.713466
H	4.391065	1.615737	1.670955
C	-3.574711	2.267734	0.525512
H	-4.596608	2.027693	0.802217
C	1.627395	-1.764214	1.729658
H	1.991712	-2.054464	2.725483
H	2.508351	-1.617738	1.097658
C	0.755004	-2.880242	1.159472
H	1.314624	-3.824959	1.173712
H	-0.118395	-3.031584	1.797209
C	-0.025216	-0.447824	2.966593
H	-0.711392	-1.295851	2.930061
H	-0.609602	0.475742	2.956045
H	0.530771	-0.501421	3.912645
C	4.535391	1.840162	-0.473333
H	5.539050	2.253810	-0.455159
C	3.861293	1.654927	-1.680510
H	4.314887	1.922348	-2.628795
H	2.024195	0.948106	-2.563260
C	1.303808	-3.055007	-1.202080
H	2.264851	-2.570575	-1.011902
H	0.983357	-2.812294	-2.218629
H	1.442792	-4.142492	-1.138195
H	-1.007485	-4.284644	-0.149182

2. TS_Mn_II_OH_H

57

E_tot= -2242.09440615 Max-Force= 0.000000 YES

Mn	0.008206	-0.325257	-0.368439
N	1.920820	0.640063	-0.484788
N	0.680969	-0.322728	1.728046

N	-2.210284	-1.109798	-0.369369
N	-1.283203	1.464948	-0.089036
N	0.337908	-2.549285	-0.101115
O	0.004525	-0.447060	-2.168202
H	-0.608898	0.130224	-2.654267
H	0.467781	-1.034992	-4.247528
C	-1.716947	3.828197	-0.210737
H	-1.338691	4.826431	-0.402808
C	-3.052249	3.608564	0.130633
H	-3.746507	4.439198	0.213435
C	-2.815868	-1.101983	-1.730734
H	-2.209692	-1.684661	-2.422206
H	-2.879189	-0.075526	-2.099974
H	-3.831230	-1.517254	-1.694990
C	-2.986814	-0.189408	0.492738
H	-2.797549	-0.440435	1.541500
H	-4.066838	-0.308515	0.335107
C	2.455613	1.060079	0.685019
C	-2.580396	1.250471	0.233734
C	-0.870052	2.731050	-0.313152
H	0.173378	2.854599	-0.587776
C	-0.943586	-3.245817	-0.417341
H	-1.017657	-3.313676	-1.504868
C	1.569919	0.873031	1.888763
H	2.161022	0.780648	2.808380
H	0.921647	1.748689	2.009269
C	-2.153604	-2.501571	0.150296
H	-3.068862	-3.054139	-0.100761
H	-2.106590	-2.461121	1.242647
C	2.621739	0.800593	-1.627694
C	3.711166	1.655307	0.746234
H	4.118823	1.975245	1.699990
C	-3.488049	2.301419	0.349853
H	-4.523863	2.096270	0.602161
C	1.500488	-1.579493	1.861622
H	1.768902	-1.734586	2.914298
H	2.430253	-1.431825	1.306532
C	0.747993	-2.784877	1.316091

```
 H        1.379814   -3.678818    1.390348
 H       -0.141066   -2.985393    1.918071
 C       -0.338012   -0.265228    2.814911
 H       -0.962645   -1.158086    2.802063
 H       -0.964233    0.618350    2.682205
 H        0.153464   -0.206280    3.793541
 C        4.431553    1.830955   -0.437714
 H        5.413593    2.293579   -0.415811
 C        3.878302    1.396070   -1.642532
 H        4.410187    1.508586   -2.581062
 H        2.139388    0.431411   -2.525320
 C        1.405660   -3.018544   -1.029409
 H        2.356445   -2.547116   -0.768990
 H        1.144963   -2.737301   -2.050212
 H        1.524894   -4.107264   -0.965003
 H       -0.926996   -4.273636   -0.031021
```

3. TS_Mn_III_O_H

```
56
E_tot= -2241.4993067 Max-Force= 0.000000 YES
Mn        0.005752   -0.329507   -0.417087
 N        1.899462    0.652035   -0.506993
 N        0.667841   -0.323460    1.708018
 N       -2.172900   -1.131404   -0.408906
 N       -1.284606    1.451420   -0.077437
 N       0.375274   -2.557902   -0.126668
 O        0.059153   -0.537198   -2.122207
 H       -0.656536    0.856405   -3.088056
 C       -1.745011    3.810672   -0.173385
 H       -1.375562    4.816155   -0.343707
 C       -3.083172    3.570202    0.142163
 H       -3.788707    4.391249    0.225231
 C       -2.764702   -1.117394   -1.778214
 H       -2.143262   -1.683082   -2.469192
```

H	-2.824987	-0.089624	-2.139786
H	-3.775964	-1.542736	-1.752133
C	-2.973302	-0.230325	0.454541
H	-2.794760	-0.491384	1.502662
H	-4.048605	-0.363949	0.279332
C	2.422300	1.083096	0.664602
C	-2.583729	1.216959	0.220104
C	-0.883490	2.725231	-0.277331
H	0.162936	2.865928	-0.531730
C	-0.898068	-3.264405	-0.453884
H	-0.962822	-3.333317	-1.542011
C	1.538336	0.884084	1.867589
H	2.132346	0.803361	2.786606
H	0.878114	1.750779	1.986944
C	-2.116470	-2.527489	0.103084
H	-3.027044	-3.079915	-0.163720
H	-2.082935	-2.494205	1.196090
C	2.606058	0.815111	-1.646268
C	3.669619	1.695825	0.728391
H	4.068343	2.023757	1.683193
C	-3.506479	2.255026	0.335533
H	-4.543699	2.033776	0.567462
C	1.504441	-1.566326	1.845189
H	1.771074	-1.720018	2.898635
H	2.434613	-1.406175	1.294083
C	0.772277	-2.782195	1.295783
H	1.414093	-3.668179	1.379276
H	-0.120666	-2.991769	1.888774
C	-0.351392	-0.279243	2.794723
H	-0.964003	-1.180556	2.782438
H	-0.990220	0.595066	2.661122
H	0.138038	-0.212790	3.774082
C	4.393795	1.877094	-0.452088
H	5.369180	2.353433	-0.426981
C	3.853680	1.427975	-1.657847
H	4.389478	1.541869	-2.593985
H	2.137796	0.431372	-2.545555
C	1.457759	-3.026519	-1.038093

```
 H        2.397968   -2.532362   -0.782062
 H        1.200776   -2.773940   -2.068199
 H        1.595568   -4.111480   -0.951674
 H       -0.877770   -4.291501   -0.065947
```

4. Mn_IV_O

```
55
E_tot= -2240.94358721 Max-Force= 0.000000 YES
Mn       -0.110720   -0.368615   -0.427101
 N        1.740902    0.532887   -0.454200
 N        0.592918   -0.391689    1.817222
 N       -2.109817   -1.051782   -0.413327
 N       -1.129517    1.389574   -0.180527
 N        0.387968   -2.428046   -0.237544
 O       -0.097755   -0.453212   -2.059190
 C       -1.449169    3.760584   -0.340735
 H       -1.044257    4.727918   -0.617407
 C       -2.742352    3.631102    0.165978
 H       -3.373721    4.503818    0.301553
 C       -2.761326   -0.923989   -1.761221
 H       -2.219995   -1.514230   -2.495438
 H       -2.736926    0.114836   -2.086420
 H       -3.799008   -1.267004   -1.682638
 C       -2.838965   -0.167483    0.542648
 H       -2.596400   -0.469814    1.565002
 H       -3.923449   -0.273301    0.424064
 C        2.275148    1.013113    0.695598
 C       -2.401081    1.254650    0.282573
 C       -0.675670    2.618351   -0.507356
 H        0.324948    2.670789   -0.917981
 C       -0.865270   -3.157644   -0.635144
 H       -0.927388   -3.128204   -1.724082
 C        1.444292    0.820362    1.936987
 H        2.087319    0.764416    2.825773
```

```
 H         0.782618    1.683617    2.076684
 C        -2.084324   -2.492462   -0.008028
 H        -3.002855   -2.998158   -0.326800
 H        -2.051489   -2.544510    1.083331
 C         2.412656    0.702522   -1.618502
 C         3.502530    1.667995    0.709448
 H         3.909754    2.032130    1.647445
 C        -3.226358    2.357602    0.470758
 H        -4.239771    2.218774    0.833730
 C         1.456576   -1.614861    1.858628
 H         1.708405   -1.874393    2.895104
 H         2.395862   -1.394700    1.346298
 C         0.755987   -2.776541    1.179811
 H         1.396662   -3.665471    1.182557
 H        -0.150944   -3.042489    1.726069
 C        -0.350734   -0.401206    2.965860
 H        -0.954506   -1.310849    2.958331
 H        -1.008970    0.468775    2.909653
 H         0.191302   -0.363440    3.919806
 C         4.194735    1.844571   -0.489987
 H         5.154117    2.353023   -0.498618
 C         3.638880    1.352623   -1.671656
 H         4.143947    1.465692   -2.624856
 H         1.919878    0.304936   -2.497991
 C         1.495248   -2.824827   -1.160442
 H         2.428916   -2.367298   -0.828828
 H         1.259809   -2.472841   -2.164169
 H         1.611782   -3.914333   -1.158475
 H        -0.797591   -4.210018   -0.333322
```

5. Mn_V_O

```
55
E_tot= -2240.94358721 Max-Force= 0.000000 YES
Mn        -0.102791   -0.359737   -0.384358
```

N	1.766884	0.487610	-0.461744
N	0.534478	-0.355468	1.760889
N	-2.133900	-1.000556	-0.434735
N	-1.091162	1.400041	-0.169002
N	0.312817	-2.443644	-0.182776
O	-0.025582	-0.570414	-2.011762
C	-1.311107	3.781756	-0.354652
H	-0.857830	4.732019	-0.618462
C	-2.631096	3.703904	0.096617
H	-3.234100	4.601608	0.201180
C	-2.720108	-0.866851	-1.823370
H	-2.189047	-1.503843	-2.526548
H	-2.652343	0.168020	-2.159687
H	-3.772401	-1.165825	-1.779486
C	-2.894670	-0.086984	0.478893
H	-2.736637	-0.396560	1.514857
H	-3.969320	-0.166835	0.281624
C	2.297497	0.977616	0.692958
C	-2.395034	1.312916	0.236869
C	-0.570056	2.614748	-0.481858
H	0.449086	2.634868	-0.845757
C	-0.959179	-3.153016	-0.598663
H	-0.990170	-3.164255	-1.689403
C	1.427398	0.837778	1.908919
H	2.030818	0.745380	2.819895
H	0.795770	1.724697	2.032161
C	-2.167162	-2.444761	-0.012174
H	-3.094029	-2.914461	-0.361018
H	-2.177311	-2.485740	1.079321
C	2.469435	0.606628	-1.621100
C	3.545430	1.588177	0.714170
H	3.948303	1.960872	1.651336
C	-3.178585	2.449672	0.384856
H	-4.212281	2.354538	0.704245
C	1.366604	-1.605516	1.903649
H	1.556929	-1.811836	2.963354
H	2.334634	-1.437096	1.426957
C	0.646243	-2.766835	1.257618

```
 H        1.267176   -3.669172    1.278236
 H       -0.276683   -3.003245    1.788844
 C       -0.475605   -0.299530    2.866427
 H       -1.093290   -1.198381    2.872604
 H       -1.103231    0.585249    2.751246
 H        0.035550   -0.235326    3.833739
 C        4.268550    1.711335   -0.476642
 H        5.246595    2.184496   -0.477486
 C        3.718209    1.211145   -1.659947
 H        4.245555    1.283103   -2.605911
 H        2.002113    0.212574   -2.515438
 C        1.441013   -2.887191   -1.075463
 H        2.374812   -2.425107   -0.753744
 H        1.225486   -2.608237   -2.107742
 H        1.539127   -3.975992   -1.007552
 H       -0.909332   -4.194614   -0.259379
```

6. TS_Mn_IV_O_OH

```
57
E_tot= -2316.67842076 Max-Force= 0.000000 YES
Mn       -0.213771   -0.358908   -0.387293
 N        1.783785    0.061310   -0.145398
 N        0.247793   -0.939774    1.853455
 N       -2.309182   -0.551742   -0.588073
 N       -0.839361    1.510995    0.142004
 N       -0.202880   -2.481086   -0.564665
 O       -0.076664   -0.171799   -2.005173
 C       -0.613564    3.875713    0.449782
 H        0.012181    4.758152    0.373801
 C       -1.928923    3.953832    0.904569
 H       -2.355477    4.905710    1.205668
 C       -2.799710   -0.025223   -1.906056
 H       -2.347635   -0.584318   -2.720871
 H       -2.511740    1.018898   -2.017678
```

H	-3.891200	-0.117437	-1.937042
C	-2.897368	0.282815	0.500142
H	-2.806251	-0.254247	1.447621
H	-3.966015	0.455837	0.327914
C	2.299923	0.192569	1.102917
C	-2.136926	1.587489	0.544495
C	-0.103442	2.640203	0.066424
H	0.896708	2.543381	-0.333791
C	-1.540999	-2.814087	-1.162635
H	-1.490210	-2.573424	-2.225939
C	1.329461	0.003882	2.238321
H	1.853558	-0.343614	3.138990
H	0.861959	0.963218	2.490733
C	-2.639880	-2.007885	-0.481061
H	-3.610743	-2.216611	-0.944580
H	-2.728989	-2.266566	0.577047
C	2.587236	0.254858	-1.217321
C	3.638458	0.505580	1.306946
H	4.024662	0.592151	2.317621
C	-2.705340	2.793124	0.936703
H	-3.745267	2.825729	1.245852
C	0.814165	-2.318043	1.701104
H	0.906492	-2.808223	2.679077
H	1.821933	-2.236392	1.287697
C	-0.058529	-3.146734	0.777163
H	0.365846	-4.148256	0.644507
H	-1.049614	-3.281888	1.214337
C	-0.769088	-0.931341	2.936889
H	-1.554307	-1.661740	2.732003
H	-1.213835	0.062930	3.018594
H	-0.314463	-1.186372	3.903131
C	4.469026	0.702156	0.201030
H	5.517498	0.947090	0.341337
C	3.932363	0.575339	-1.078864
H	4.538810	0.724199	-1.965344
H	2.104670	0.165593	-2.181459
C	0.872803	-2.960936	-1.485138
H	1.848452	-2.798297	-1.023771

```
 H         0.817635   -2.395837   -2.414892
 H         0.745980   -4.031121   -1.683829
 H        -1.734639   -3.890073   -1.072224
 O         1.539203    2.737932   -2.743514
 H         1.388891    3.097349   -3.646418
```

7. Mn_III_OOH

```
57
E_tot= -2316.71970579 Max-Force= 0.000000 YES
Mn         0.014218   -0.258445   -0.279297
 N        1.879091    0.766618   -0.422513
 N         0.683195   -0.132962    1.834208
 N        -2.064745   -1.278113   -0.248221
 N        -1.436742    1.403573    0.007377
 N         0.581107   -2.484383    0.113440
 O        -0.171928   -0.007286   -2.077219
 C        -2.140492    3.685096   -0.266051
 H        -1.874522    4.711048   -0.496354
 C        -3.455303    3.322422    0.027386
 H        -4.246106    4.066274    0.034522
 C        -2.649606   -1.363295   -1.617846
 H        -2.008937   -1.966969   -2.259360
 H        -2.730287   -0.365122   -2.047439
 H        -3.643860   -1.824708   -1.569780
 C        -2.949266   -0.418171    0.581026
 H        -2.738726   -0.611994    1.637374
 H        -4.004688   -0.673132    0.420999
 C         2.377758    1.286450    0.723807
 C        -2.713458    1.048074    0.275569
 C        -1.165037    2.694571   -0.272359
 H        -0.133512    2.928596   -0.518249
 C        -0.623668   -3.304643   -0.201306
 H        -0.662609   -3.420952   -1.286893
 C         1.491381    1.123655    1.929586
```

H	2.075542	1.125492	2.858271
H	0.789946	1.963681	1.989076
C	-1.905281	-2.647949	0.313256
H	-2.766844	-3.277631	0.055472
H	-1.890925	-2.572999	1.404124
C	2.572207	0.916278	-1.572678
C	3.592574	1.962569	0.755769
H	3.969015	2.364609	1.691072
C	-3.745355	1.983429	0.293899
H	-4.761749	1.666708	0.506185
C	1.585688	-1.316428	2.053128
H	1.837012	-1.394690	3.118472
H	2.516550	-1.132871	1.511264
C	0.936209	-2.598480	1.560021
H	1.618140	-3.442871	1.721585
H	0.036588	-2.816900	2.139058
C	-0.348803	-0.081469	2.908941
H	-0.908243	-1.016217	2.945324
H	-1.034136	0.745651	2.719151
H	0.127761	0.069202	3.885182
C	4.310717	2.114430	-0.432541
H	5.262242	2.637370	-0.432984
C	3.791802	1.582772	-1.613263
H	4.320124	1.678757	-2.555574
H	2.123491	0.488062	-2.460430
C	1.732896	-2.952636	-0.709999
H	2.628716	-2.382831	-0.451588
H	1.514324	-2.798747	-1.765785
H	1.930769	-4.016530	-0.527119
H	-0.529610	-4.312133	0.226461
O	0.350488	-1.115583	-2.837712
H	-0.262535	-1.117267	-3.598278

8. TS_Mn_III_OO_H

```
57
E_tot= -2316.60200142 Max-Force= 0.000000 YES
Mn       -0.032058   -0.251820   -0.198839
N         1.991815    0.603855   -0.518331
N         0.847097   -0.226823    1.890945
N        -2.275062   -0.984500   -0.165811
N        -1.241580    1.591880    0.000089
N         0.241715   -2.503182    0.102077
O        -0.187185   -0.146193   -2.296202
C        -1.645970    3.947287   -0.270036
H        -1.256578    4.925895   -0.528935
C        -2.980161    3.768429    0.096159
H        -3.662550    4.612196    0.130451
C        -2.974751   -0.997501   -1.480432
H        -2.508824   -1.714103   -2.157156
H        -2.926316   -0.007318   -1.937989
H        -4.027986   -1.277536   -1.349388
C        -2.946266    0.003266    0.717045
H        -2.651501   -0.200064    1.752830
H        -4.038533   -0.099777    0.674733
C         2.630593    0.969932    0.619745
C        -2.537919    1.417761    0.351512
C        -0.814307    2.834001   -0.309381
H         0.227401    2.925972   -0.602730
C        -1.076090   -3.164357   -0.146595
H        -1.184493   -3.282258   -1.228349
C         1.830031    0.892199    1.899243
H         2.499695    0.808527    2.765523
H         1.263982    1.823157    2.026042
C        -2.246452   -2.354682    0.415108
H        -3.183412   -2.890463    0.212444
H        -2.168479   -2.267309    1.503034
C         2.651508    0.725061   -1.691913
C         3.937695    1.450622    0.609733
H         4.421078    1.725607    1.541941
C        -3.431323    2.484348    0.406230
H        -4.466583    2.311147    0.682851
C         1.556440   -1.541680    1.998264
```

H	1.875564	-1.716375	3.034511
H	2.461788	-1.488560	1.387555
C	0.670571	-2.688904	1.525234
H	1.207422	-3.639468	1.636440
H	-0.218605	-2.760866	2.154792
C	-0.075836	-0.040260	3.042541
H	-0.773665	-0.876347	3.109679
H	-0.640533	0.885817	2.914447
H	0.482356	0.014699	3.986024
C	4.609239	1.576354	-0.606842
H	5.628019	1.950589	-0.635477
C	3.951596	1.208444	-1.780422
H	4.433236	1.287331	-2.748996
H	2.112551	0.428461	-2.584454
C	1.268005	-3.090593	-0.804159
H	2.244630	-2.643863	-0.604002
H	0.999754	-2.895578	-1.844515
H	1.343272	-4.175859	-0.660240
H	-1.085416	-4.175136	0.282947
O	-0.220138	-1.148691	-3.024762
H	-3.554751	-4.700913	-2.084309

9. Mn_IV_OO

56

E_tot= -2316.17124558 Max-Force= 0.000000 YES

Mn	-0.027133	-0.269182	-0.216553
N	1.942124	0.720909	-0.483472
N	0.827679	-0.258076	1.882190
N	-2.219901	-1.143250	-0.231411
N	-1.356505	1.486259	0.021676
N	0.382771	-2.509737	0.016175
O	-0.170947	-0.094787	-2.308299
C	-1.909067	3.817563	-0.187731
H	-1.581302	4.825928	-0.415961

C	-3.231787	3.543694	0.160882
H	-3.967098	4.340844	0.212159
C	-2.903492	-1.159638	-1.554545
H	-2.383243	-1.820510	-2.248378
H	-2.916415	-0.154075	-1.979439
H	-3.937080	-1.513025	-1.445605
C	-2.961960	-0.228289	0.672911
H	-2.664656	-0.443843	1.705383
H	-4.044828	-0.399777	0.614622
C	2.544584	1.090418	0.673095
C	-2.641921	1.219722	0.354357
C	-1.007323	2.761330	-0.249240
H	0.028676	2.927913	-0.529542
C	-0.888582	-3.244304	-0.267187
H	-0.979013	-3.333511	-1.353342
C	1.738673	0.918845	1.939955
H	2.404129	0.847025	2.810496
H	1.114546	1.807911	2.091727
C	-2.111802	-2.526224	0.307480
H	-3.013397	-3.110845	0.081033
H	-2.047382	-2.467678	1.398214
C	2.603898	0.922892	-1.644928
C	3.817429	1.655471	0.693943
H	4.272733	1.930898	1.640057
C	-3.602257	2.225086	0.430346
H	-4.626564	1.978240	0.691422
C	1.616150	-1.529379	1.957727
H	1.933313	-1.716944	2.992276
H	2.523661	-1.400361	1.361666
C	0.809128	-2.713783	1.437520
H	1.404119	-3.631719	1.524815
H	-0.079656	-2.862140	2.054206
C	-0.118716	-0.165702	3.026372
H	-0.764094	-1.044842	3.058486
H	-0.738105	0.727410	2.918666
H	0.423848	-0.106085	3.978621
C	4.490808	1.864329	-0.509956
H	5.483011	2.305117	-0.514806

```
 C        3.870166    1.492677   -1.702388
 H        4.355091    1.634546   -2.662106
 H        2.094275    0.620861   -2.552653
 C        1.453380   -3.000097   -0.896284
 H        2.395761   -2.495114   -0.671636
 H        1.182102   -2.791342   -1.933314
 H        1.600013   -4.081820   -0.784083
 H       -0.838233   -4.266771    0.130687
 O       -0.128169   -1.069856   -3.072941
```

10. TS_Mn_II_OO

```
56
E_tot= -2316.054380588 Max-Force= 0.000000 YES
Mn       -0.018284    0.277263    0.061391
 N        1.832889   -0.898150    0.407871
 N        1.089099    0.544123   -1.899142
 N       -2.091021    1.319518    0.264873
 N       -1.490316   -1.316230   -0.363678
 N        0.612911    2.469477    0.326730
 O       -0.968324   -0.817501    3.651317
 C       -2.265884   -3.588344   -0.506685
 H       -2.038990   -4.646514   -0.434915
 C       -3.551746   -3.138991   -0.808289
 H       -4.358763   -3.845083   -0.978426
 C       -2.775667    1.208507    1.580668
 H       -2.180743    1.681771    2.362620
 H       -2.914124    0.156774    1.838966
 H       -3.759472    1.695112    1.546847
 C       -2.909014    0.623151   -0.761638
 H       -2.572444    0.951500   -1.753150
 H       -3.969871    0.895586   -0.682919
 C        2.545499   -1.116642   -0.726436
 C       -2.739798   -0.880860   -0.654055
 C       -1.268057   -2.645252   -0.288347
```

H	-0.255132	-2.950056	-0.041754
C	-0.603500	3.275118	0.648886
H	-0.750923	3.232362	1.731388
C	1.918508	-0.682055	-2.035699
H	2.697489	-0.542994	-2.797546
H	1.262304	-1.482240	-2.400665
C	-1.844923	2.748114	-0.073111
H	-2.711003	3.372897	0.184272
H	-1.716858	2.824736	-1.157756
C	2.350054	-1.331804	1.579489
C	3.780308	-1.762095	-0.707109
H	4.327191	-1.910401	-1.633008
C	-3.791142	-1.765355	-0.878054
H	-4.782966	-1.384812	-1.101126
C	1.953339	1.742847	-1.666638
H	2.379141	2.095546	-2.615720
H	2.791986	1.438646	-1.034238
C	1.177524	2.876102	-0.998166
H	1.834223	3.747918	-0.878080
H	0.354985	3.194717	-1.643289
C	0.273798	0.712851	-3.130354
H	-0.312278	1.632546	-3.072514
H	-0.409820	-0.133307	-3.237654
H	0.909485	0.768282	-4.023862
C	4.299064	-2.213869	0.506189
H	5.258581	-2.720855	0.538870
C	3.567871	-1.994295	1.673062
H	3.932087	-2.322109	2.640673
H	1.762398	-1.134289	2.468256
C	1.635527	2.662193	1.391164
H	2.539906	2.099702	1.148812
H	1.247464	2.299983	2.346852
H	1.901157	3.721766	1.499685
H	-0.448139	4.332339	0.395011
O	-0.249837	-0.083522	3.001653

6

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