



**CHAPTER-1**

**Brief Introduction to Computational  
Chemistry**

### [1.1] Introduction

Chemistry is a scientific discipline which deals with the study of matter, their properties (both physical and chemical) and reactions which involves breaking and formation of bonds between chemical entities. Even though from its beginning, chemistry relies on experimental aspects, nowadays due to the tremendous development in modern computing techniques, computational chemistry emerges as an important tool towards solving a variety of chemical problems. Computational chemistry is based on methods which use the law of quantum mechanics and is found to be very helpful in the study of different properties such as molecular geometry, relative energies of isomers, simulation of spectroscopic properties as well as to investigate reaction pathways, intermediates and transition states etc. The methods used by a computational program can be broadly classified into five categories [1] which are as follows:

- (a) Molecular mechanics
- (b) *Ab initio*
- (c) Semiempirical
- (d) Density functional theory
- (e) Molecular dynamics

Molecular mechanics considers a molecule as balls and springs model while *Ab initio* and semiempirical methods are known as wavefunction methods as they deal with the solving of Schrödinger equation considering the wavefunction for a particular state. Further, molecular dynamics is based on laws of motion. However, the works presented in this thesis were being carried out employing Density Functional Theory (DFT) [2] calculations using the Gaussian software package [3] and accordingly, a brief description of DFT is provided below.

### [1.2] Density Functional Theory

Unlike wavefunction methods, DFT relies on electron density function and uses the electron density (denoted by  $\rho(x, y, z)$  where  $x, y, z$  are the spatial coordinates) of a particular system to determine its properties. An alternative notation for  $\rho(x, y, z)$  is  $\rho(\mathbf{r})$  where  $\mathbf{r}$  is the position vector of the point with coordinates  $(x, y, z)$ . Being a function of only position, i.e., it depends only on the spatial variables  $(x, y, z)$ , DFT is advantageous over the wavefunction methods as the later depends not only on spatial variables but also on spin variable thereby creating problems in the solution of multi-atom systems. The use of electron density as the basis for determination of atomic and molecular properties

of a system was initiated as early as in 1927 by Enrico Fermi and P. A. M. Dirac [4]. Similarly, the  $X_\alpha$  method which was introduced by Slater in 1951 was also based on model comprising of uniform electron gas [5]. However, current DFT methods are based on the two theorems put forwarded by Hohenberg and Kohn in 1964 [2c].

### [1.2.1] The Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem [2c] can be stated as – *The ground state electron density function  $\rho_0(r)$  determines all the properties of a molecule in its ground electronic state.* Alternatively, any ground state property of a molecule is a functional of  $\rho_0(r)$ . For example, the ground state energy ( $E_0$ ) of a molecule can be represented as

$$E_0 = F[\rho_0(r)] \quad (1.1)$$

where  $F[\rho_0(r)]$  is the functional corresponding to the ground state electronic energy. It should be noted that a functional is a function of a definite function.

The second Hohenberg-Kohn theorem [2c] states that *the energy obtained from any trial electron density function will be higher than (or equal to, if the respective function represents the true electron density) the true ground state energy.* Mathematically it can be represented as

$$E_v[\rho_t(r)] \geq E_0[\rho_0(r)] \quad (1.2)$$

where  $\rho_t(r)$  is a trial electron density while  $\rho_0(r)$  is the true ground state electron density of the molecule. However, the validity of the second Hohenberg-Kohn theorem relies on the fact that the trial electron density must obey the conditions represented by the equations (1.3) and (1.4).

$$\int \rho_t(r) dr = N \quad (1.3)$$

where N is the number of total electrons in the molecule. For all the values of r,

$$\rho_t(r) \geq 0 \quad (1.4)$$

### [1.2.2] The Kohn-Sham Energy

The calculation of the total energy of a molecule in Kohn-Sham (KS) approach is carried out in a similar way to those of the Hartree-Fock approach used in the wavefunction theory. An initial guess of the electron density is used to determine the initial guess of the KS orbitals which is then refined in order to get the final KS orbitals and the final electron density. The total ground state energy ( $E_0$ ) comprises of three

energy terms *viz.*, electron kinetic energy, nucleus-electron attraction energy and electron-electron repulsion energy and each of these three energies is a functional of the ground state electron density.

$$E_0 = \langle T[\rho_0(r)] \rangle + \langle V_{Ne}[\rho_0(r)] \rangle + \langle V_{ee}[\rho_0(r)] \rangle \quad (1.5)$$

The functional corresponding to the nucleus-electron attraction energy can be expressed in terms of electron density and external potential ( $v(r)$ ) as [6]:

$$\langle V_{Ne}[\rho_0(r)] \rangle = \int \rho_0(r)v(r)dr \quad (1.6)$$

Therefore, equation (1.5) will take the form:

$$E_0 = \int \rho_0(r)v(r)dr + \langle T[\rho_0(r)] \rangle + \langle V_{ee}[\rho_0(r)] \rangle \quad (1.7)$$

In order to determine the unknown functionals corresponding to the electron kinetic energy and electron-electron repulsion energy in equation (1.7), Kohn and Sham introduced two new quantities  $\Delta\langle T[\rho_0(r)] \rangle$  and  $\Delta\langle V_{ee}[\rho_0(r)] \rangle$ .  $\Delta\langle T[\rho_0(r)] \rangle$  is nothing but the deviation of real kinetic energy from the kinetic energy of a reference system consisting of non-interacting electrons:

$$\Delta\langle T[\rho_0(r)] \rangle = \langle T[\rho_0(r)] \rangle - \langle T_r[\rho_0(r)] \rangle \quad (1.8)$$

Similarly,  $\Delta\langle V_{ee}[\rho_0(r)] \rangle$  is the deviation of the real electron-electron repulsion energy from a classical charge-cloud coulomb repulsion energy and can be mathematically defined as:

$$\Delta\langle V_{ee}[\rho_0(r)] \rangle = \langle V_{ee}[\rho_0(r)] \rangle - \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} dr_1 dr_2 \quad (1.9)$$

Therefore, using equations (1.7), (1.8) and (1.9), the ground state energy can be given as:

$$E_0 = \int \rho_0(r)v(r)dr + \langle T_r[\rho_0(r)] \rangle + \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} dr_1 dr_2 + \Delta\langle T[\rho_0(r)] \rangle + \Delta\langle V_{ee}[\rho_0(r)] \rangle \quad (1.10)$$

Or,

$$E_0 = \int \rho_0(r)v(r)dr + \langle T_r[\rho_0(r)] \rangle + \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} dr_1 dr_2 + E_{XC}[\rho_0(r)] \quad (1.11)$$

where  $E_{XC}[\rho_0(r)]$  is the exchange-correlation energy functional and it is the sum of the energy deviations represented by the equations (1.8) and (1.9). Further simplification of the first two energy terms in equation (1.11) leads to the following expression for the total ground state electronic energy:

$$E_0 = - \sum_{\text{nuclei } A} Z_A \int \frac{\rho_0(r_1)}{r_{1A}} dr_1 - \frac{1}{2} \sum_{i=1}^{2n} \langle \psi_i^{\text{KS}}(1) | \nabla_1^2 | \psi_i^{\text{KS}}(1) \rangle + \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} dr_1 dr_2 + E_{\text{XC}}[\rho_0(r)] \quad (1.12)$$

Therefore, the only term which contains the unknown functional is the fourth term in the above equation that is the exchange correlation energy  $E_{\text{XC}}[\rho_0(r)]$ . Further, the true ground state electron density which is same as that of the non-interacting reference system can be expressed in terms of KS spatial orbitals ( $\psi_i^{\text{KS}}$ ) as follows:

$$\rho_0 = \rho_r = \sum_{i=1}^{2n} |\psi_i^{\text{KS}}(1)|^2 \quad (1.13)$$

Now, using the equations (1.12) and (1.13) as well as considering the variation principle as suggested by the second Hohenberg-Kohn theorem, the final KS equation can be written as:

$$\left[ -\frac{1}{2} \nabla_1^2 - \sum_{\text{nuclei } A} \frac{Z_A}{r_{1A}} + \int \frac{\rho(r_2)}{r_{12}} dr_2 + v_{\text{XC}}(1) \right] \psi_i^{\text{KS}}(1) = \epsilon_i^{\text{KS}} \psi_i^{\text{KS}}(1) \quad (1.14)$$

where  $v_{\text{XC}}(1)$  is the exchange-correlation potential designated for electron number 1. It can be defined as the functional derivative of the exchange-correlation energy functional with respect to the electron density functional:

$$v_{\text{XC}}(r) = \frac{\delta E_{\text{XC}}[\rho(r)]}{\delta \rho(r)} \quad (1.15)$$

If one can exactly determine the exchange-correlation functional, the exact energy of a system can be determined. However, this is the main problem with DFT that the exact functional and hence the corresponding potential are not known. Current DFT methods comprise of a variety of approximations for the exchange-correlation functional and a brief account of them is discussed below.

### [1.2.3] The Local Density Approximation (LDA)

It is the simplest approximation to the exchange-correlation energy functional and for a particular point it depends only on the electron density at that point. For a homogeneous electron gas model, the exchange-correlation energy functional

$E_{XC}^{LDA}[\rho(r)]$  and the associated potential  $v_{XC}^{LDA}(r)$  can be accurately calculated and given by:

$$E_{XC}^{LDA}[\rho(r)] = \int \rho(r) \epsilon_{XC}[\rho(r)] dr \quad (1.16)$$

where  $\epsilon_{XC}[\rho(r)]$  is the exchange-correlation energy per particle.

$$v_{XC}^{LDA}(r) = \frac{\delta E_{XC}^{LDA}[\rho(r)]}{\delta \rho(r)} = \epsilon_{XC}[\rho(r)] + \rho(r) \frac{\delta \epsilon_{XC}[\rho(r)]}{\delta \rho(r)} \quad (1.17)$$

An extended version of the simple LDA approximation is the local spin density approximation (LSDA) where the electrons with different spins ( $\alpha$  and  $\beta$ ) are assigned in different spatial orbitals. Therefore, LSDA is found to be suitable for systems having unpaired electrons, radicals etc. The exchange-correlation energy functional  $E_{XC}^{LSDA}[\rho_{\alpha}, \rho_{\beta}]$  is given by:

$$E_{XC}^{LSDA}[\rho_{\alpha}, \rho_{\beta}] = \int \rho(r) \epsilon_{XC}[\rho_{\alpha}, \rho_{\beta}] dr \quad (1.18)$$

However, LSDA is equivalent to LDA for systems in which all the electrons are paired. Even though LDA is found to be reasonably good in the prediction of a variety of properties, it has several demerits. For example, LDA performs poorly in the determination of ionization potential, dissociation energies, energy barriers etc. Therefore, further modification of LDA was carried out which lead to the evolution of more sophisticated approximations to the exchange-correlation energy functional.

#### [1.2.4] The Generalized-Gradient Approximation (GGA)

In case of LDA (also in LSDA), the system is considered to be composed of homogeneous electron gas, i.e., the distribution of electron density is equal throughout the whole system. However, this is not the case with real molecules where the electron density varies with spatial coordinates. Therefore, LDA functionals are improved by introducing the gradient of the electron density which is the first derivative of electron density with respect to position. This is known as generalized-gradient approximation and the functionals are called gradient-corrected functionals. The exchange-correlation energy functional can be written as:

$$E_{XC}^{GGA}[\rho(r)] = \int \rho(r) \epsilon_{XC}[\rho(r), |\nabla \rho(r)|] dr \quad (1.19)$$

The use of GGA functionals instead of the LDA functional leads to better results with more accuracy. B88 [7], LYP [8] and PW91 [9] are the examples of GGA functional.

A more sophisticated version of GGA functionals are the meta-GGA functionals in which the exchange-correlation energy functional ( $E_{XC}^{mGGA}$ ) is not only a function of electron density ( $\rho(r)$ ) and its first derivative ( $\nabla\rho(r)$ ) but also of the second derivative of electron density ( $\nabla^2\rho(r)$ ) and/or local kinetic energy density ( $\tau$ ). TPSS [10] and M06-L [11] are examples of meta-GGA functional. Mathematically,  $E_{XC}^{mGGA}$  can be expressed as:

$$E_{XC}^{mGGA}[\rho(r)] = \int \rho(r) \epsilon_{XC}[\rho(r), |\nabla\rho(r)|, \nabla^2\rho(r), \tau] dr \quad (1.20)$$

where the local kinetic energy density is given by:

$$\tau = \frac{1}{2} \sum_i |\nabla\psi_i(r)|^2 \quad (1.21)$$

### [1.2.5] Hybrid Functional

Hybrid functionals are those in which the exchange-correlation energy functional includes an exact exchange energy ( $E_X^{HF}$ ) calculated using Hartree-Fock theory and is given by the following expression:

$$E_X^{HF} = - \sum_{i=1}^n \sum_{j=1}^n \langle \psi_i^{KS}(1) \psi_j^{KS}(2) \left| \frac{1}{r_{ij}} \right| \psi_i^{KS}(2) \psi_j^{KS}(1) \rangle \quad (1.22)$$

The contribution of the exchange functional to the total exchange-correlation functional is significantly larger than the contribution from the correlation part. Further,  $E_X^{HF}$  gives the exact exchange energy for a non-interacting reference system having electron density equal to the real system. Therefore, it will be wise to use hybrid functionals for the calculation of energy (and the associated properties) of a molecular system in order to get more accurate results. A widely used hybrid functional is B3LYP [12] which is constructed by introducing the LYP 1988 correlation functional [8] to that in the Becke 1993 exchange-energy functional [13].

### [1.3] Basis Set

A basis set is a set of mathematical functions (called basis functions) used to approximate the atomic orbitals of an atom and the linear combinations of these basis functions yield the molecular orbitals. It is worthwhile to mention that accuracy as well as the computational cost efficiency of a particular calculation is largely governed by the

type of basis set used. The basis functions are of two types – Slater type functions [14] and Gaussian type functions [15] and can be represented by the following expressions:

$$\varphi_{ST} = Ne^{(-\alpha r)} \quad (1.23)$$

$$\varphi_{GT} = Ne^{(-\alpha r^2)} \quad (1.24)$$

Therefore, Gaussian type functions differ from Slater type functions in the fact that the exponential part in the former involves the square of the radius ( $r^2$ ) while the later involves only 'r'. Unfortunately, evaluation of certain integrals is very difficult with Slater type functions whereas they can be easily evaluated with Gaussian type functions. However, the major drawback of Gaussian type functions is that they describe less satisfactorily the radial electron distribution thereby leading to results with less accuracy. To overcome this problem, a number of Gaussian type functions with different exponents and coefficients are summed up to approximate a particular Slater type function.

The basis sets are broadly classified into two categories known as *minimal* basis sets and *extended* basis sets. *Minimal* basis sets are the simplest ones and describe only the basic characteristics of a particular orbital. STO-3G [16] is an example of *minimal* basis set which is constructed by the combination of three Gaussian functions to approximate one Slater type function/orbital. *Extended* basis sets are more sophisticated than the *minimal* ones and hence they give more clear and accurate approximation for each atomic orbital. A brief description of different types of *extended* basis set is given below.

In case of *minimal* basis sets, all the orbitals are approximated to be similar *i.e.*, all the orbitals are represented by only one type of Slater function. However, in case of real molecules, all the orbitals are not equivalent. Therefore, to get a better picture of the atomic orbitals, they must be represented with more than one basis function for each orbital. For example, in case of *double zeta* basis set, each orbital is described by two Slater type functions having different orbital exponent. Similarly, *triple zeta* basis set describes an orbital by a combination of three Slater type functions. cc-pVDZ and cc-pVTZ are examples of *double zeta* and *triple-zeta* basis sets respectively [17].

Another class of extended basis set is the *split valence* basis set where the core and valence shell orbitals are described with different types of basis functions. 6-31G is an example of *split valence double-zeta* basis set where the core and valence orbitals are represented by one and two different types of Slater type basis functions respectively. "6" indicates that the Slater function representing the core orbitals is obtained by the



summation of six Gaussian functions. Similarly, “3” and “1” stands for the number of Gaussian functions summed up to obtain the first and second Slater functions representing the valence orbitals (i.e., of *double zeta*).

In case of the molecules, the atomic orbitals undergo polarization because of the interaction between the neighbouring atoms. As a result of this polarization, the “s” orbitals attain somewhat “p” character and similarly the “p” orbitals attain “d” character. Therefore, *polarized* basis sets were developed where polarization functions are added to the pure atomic orbitals. For example, 6-31G\* is an example of *polarized* basis set where the single asterisk ‘\*’ indicates that the polarization has been taken into account in the “p” orbitals for all the non-hydrogen atoms. Similarly, use of two asterisks ‘\*\*’ (e.g., 6-31G\*\*) mean that the polarization of the “s” orbitals is also considered in addition to the “p” orbitals. One alternative notation for representing the polarized basis set is by putting the higher angular momentum orbitals within parenthesis. For example, 6-31G\* and 6-31G\*\* basis sets can also be represented as 6-31G(d) and 6-31G(d,p) respectively.

Even though the basis sets discussed till now are found to be suitable for various systems, they give poor results in case of molecules having lone pairs, anions, excited electronic states etc. Therefore, *diffuse* functions were developed which can effectively describe the orbitals for systems having loosely bound electrons. Due to the very small exponent values, *diffuse* functions fall very slowly with the increase in distance from the nucleus. Therefore, they can accurately approximate the orbitals with significant electron density at relatively large distances from the nucleus. Typically, a basis set with *diffuse* functions is represented by plus ‘+’ signs. One ‘+’ sign (e.g., 6-31+G\*) indicates that the diffuse function is added to all the heavy (non-hydrogen) atoms while two ‘++’ signs (e.g., 6-31++G\*) are for the heavy atoms as well as for the hydrogen atoms.

### [1.4] Effective Core Potential (ECP)

In case of the molecules containing heavy atoms (third row onwards), the use of all electron basis sets takes very long time for any calculations which is due to the presence of a large number of two-electron integrals. Further, for the heavier atoms, relativistic effects also induce complications. The only way to overcome these problems without compromising with the accuracy of the results is to replace the core electrons in a calculation with an average potential. This is known as effective core potential (ECP) [18] or pseudopotential (PP) and can be expressed by the following general expression:

$$\text{ECP}(r) = \sum_{i=1}^k c_i r^{n_i} e^{-\alpha_i r^2} \quad (1.25)$$

where the summation is over  $k$  terms,  $c_i$  is the coefficient characteristic of each term,  $r$  is the distance from the nucleus and  $\alpha_i$  is an exponent for the  $i^{\text{th}}$  term. ECPs can be broadly divided as: large-core, small-core and all-electron ECPs. Use of ECP eliminates the need of evaluation of the two-electron integrals for the core electrons thereby significantly reduces the total time of computation for a particular calculation. Since the chemical property of a species is mainly governed by the valence electrons, therefore use of ECP for the core electrons does not alter the property of the same. Indeed, use of ECP for the heavier atoms, mostly for transition metals is found to be beneficial as it accounts for the relativistic effects and also found to reproduce experimental results. However, there are some limitations of ECP such as the inability to describe properties of a system which directly relates to the core electrons (*e.g.*, X-ray photoelectron spectroscopy). LANL2DZ is an example of popular basis set which include ECP for the core electrons [19].

### [1.5] Gauge-Independent Atomic Orbital (GIAO) Method

Gauge-Independent Atomic Orbital (GIAO) method is used to calculate the NMR shielding tensors. GIAO approach uses local gauge origins to define the vector potential of the external magnetic field [20]. It was first adapted by Ditchfield in the gauge invariant atomic orbitals (GIAO) method which was followed by Giessner-Prettre and Fukui [21-23]. In various applications, GIAO method appears to provide high accuracy with a smaller basis and has been found to be successful in the determination of the magnetic properties of various chemical entities.

### [1.6] Quantum Theory of Atoms in Molecules (QTAIM)

QTAIM is a very powerful tool to interpret and understand the observations of experimental chemistry as it provides the quantum basis for an atom in a molecule [24]. The discovery of QTAIM helps in solving a number of problems at atomic level which were previously not possible by any other methods. QTAIM considers an atom in a molecule as a region of real space bounded by a surface  $S(r_s)$  of local zero-flux in the gradient vector field of the electron density  $\rho(r)$  and expressed by the following equation [25]:

$$\nabla\rho(r) \cdot n(r) = 0 \quad \forall r \in S(r_s) \quad (1.26)$$

where  $\mathbf{n}(\mathbf{r})$  is a unit vector perpendicular to the surface. This equation defines the boundary condition for an atom in a molecule as well as leads to the partitioning of a molecular system into a set of separate non-overlapping atoms.

In a molecule, the nuclei of two bonded atoms are linked by a *bond path* along which the electron density is maximum with respect to any other neighbouring line. There exists a point known as *bond critical point (bcp)* along the bond path where the first derivative of electron density is zero (i.e.,  $\nabla\rho(\mathbf{r})=0$ ). At the *bond critical point*,  $\rho(\mathbf{r})$  falls down in two perpendicular directions of space while rises in the third direction. Accordingly, *bcp* possesses two negative ( $\lambda_1$  and  $\lambda_2$ ) and one positive curvature ( $\lambda_3$ ) and the laplacian of electron density [ $\nabla^2\rho(\mathbf{r})$ ] at the *bcp* is the summation of all these three curvatures.

$$\nabla^2\rho(\mathbf{r}) = \lambda_1 + \lambda_2 + \lambda_3 \quad (1.27)$$

The laplacian of electron density provides a measure of local charge concentration or depletion. A positive value of [ $\nabla^2\rho(\mathbf{r})$ ] indicates local charge depletion whereas a negative value indicates charge concentration. A critical point (CP) is expressed by its rank and signature where rank is the number of non-zero curvatures of  $\rho(\mathbf{r})$  at the CP and the signature is the algebraic sum of their signs [25]. Therefore, a *bcp* can be expressed as (3, -1) where 3 and -1 are the rank and signature respectively. There are three more types of CPs which are as follows:

(a) (3, -3) CP: This is known as *nuclear critical point (ncp)* where the electron density falls down in all the three perpendicular directions of space, i.e., all the three curvatures are negative.

(b) (3, +1) CP: In this case, electron density rises in two directions while falls in one directions, i.e., two curvatures are positive and one is negative. This type of critical point is known as *ring critical point (rcp)* which resides in the middle of several bonds forming a ring.

(c) (3, +3) CP: Here all the curvatures are positive as electron density rises in all the three perpendicular directions of space. This is a local minimum and known as *cage critical point (ccp)* because these types of CPs are found when a number of rings form a cage structure.

A brief description of the topological parameters which were evaluated in order to study the objectives of this thesis is given below.

### [1.6.1] Bond Magnetizability

QTAIM can be successfully applied to determine the extent of aromaticity within a system by the determination of magnetic response properties such as inter-atomic magnetizability or bond magnetizability [26]. The bond magnetizability values gives a direct measure of the current flux between two adjacent atomic basins and hence to predict the extent of electron delocalization within a ring system. The magnetizability tensor ( $\chi$ ) of a system in an external magnetic field (B) is given by [27]

$$\chi = \left( \frac{1}{2cB} \right) \int \mathbf{r} \times \mathbf{J}(\mathbf{r}) d\mathbf{r} \quad (1.28)$$

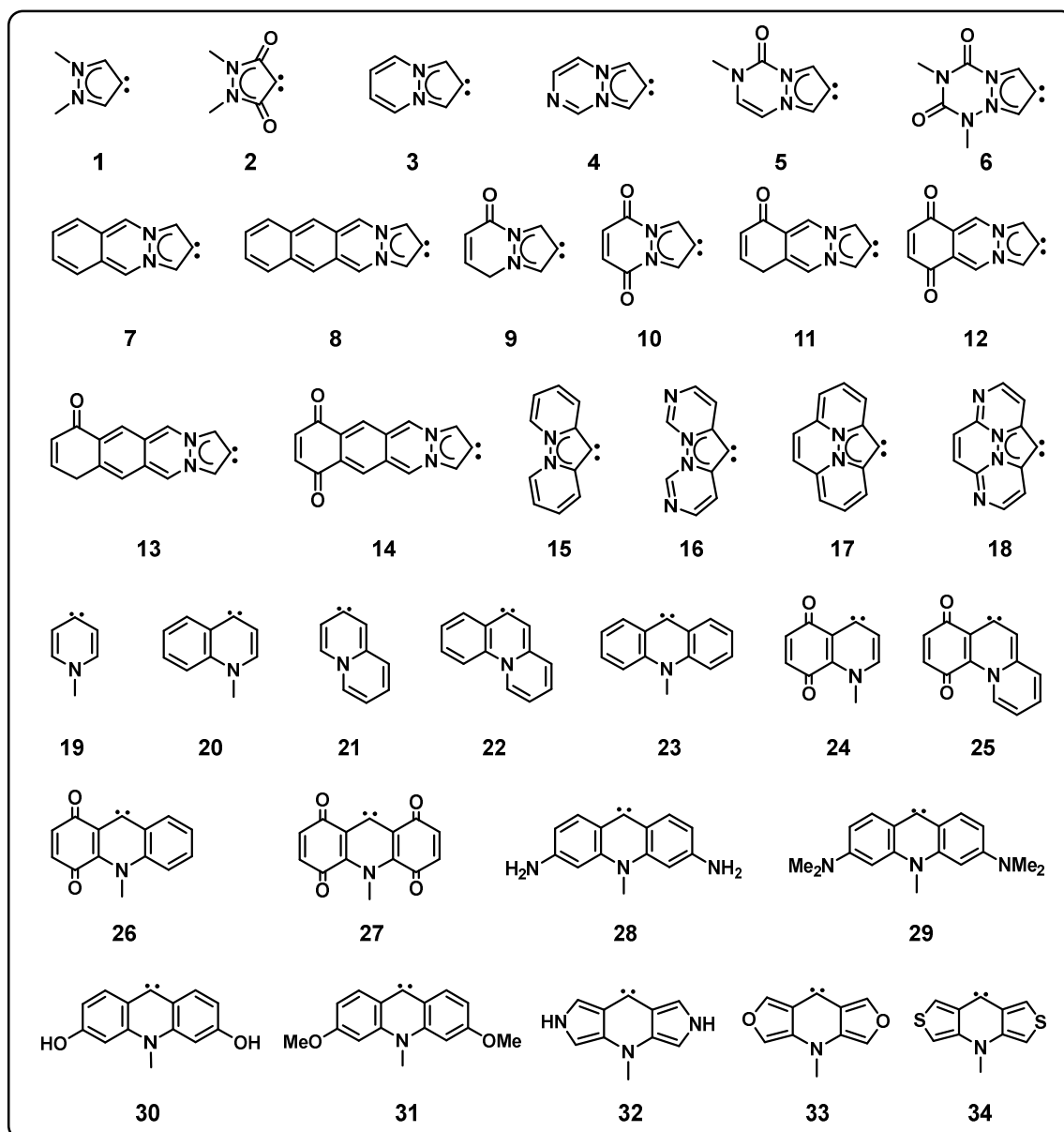
where  $\mathbf{J}(\mathbf{r})$  is the induced current density. For an atomic basin defined by the equation (1.26), the magnetizability which arises due to the flow of current density within the atomic basin is termed as intra-atomic magnetizability. However, flow of current density flux through the interatomic surfaces between the atoms and its adjacent neighbours gives the inter-atomic magnetizability. Therefore, the total magnetizability obtained for any system has contributions from both intra- and inter-atomic magnetizabilities. It is worthwhile to mention that in case of ionic and polar systems, the contribution of bond-magnetizability to the total magnetizability is very less while the same predominates in case of covalently bonded ones [28].

## [1.7] Brief Overview of the Remaining Chapters

### [1.7.1] Chapter 2: Tuning the Electronic and Ligand Properties of Remote Carbenes.

*N*-Heterocyclic carbenes (NHCs) have found a great deal of attention after their isolation by Arduengo in 1991 [29] and have grown extensively in the past few years because of the remarkable catalytic activity of the corresponding transition metal complexes. NHCs are found to have excellent  $\sigma$ -donation as well as considerable  $\pi$ -acceptance abilities [30,31]. In addition to these NHCs, NHC variants known as remote NHCs (rNHCs) have drawn the attention of several researchers as rNHCs are better  $\sigma$ -donors as well as better  $\pi$ -acceptors than their normal NHC counterparts [32]. Interestingly, annulation and/or carbonylation of the NHC ligands were found to significantly increase their  $\pi$ -accepting abilities [33].

In this chapter, the effect of annulation and carbonylation on the electronic and ligating properties of both five- and six-membered rNHCs (Scheme 1.1) were studied



**Scheme 1.1:** Schematic representation of the mesoionic (1–18) and remote NHCs (19–34) considered in this study.

employing PBE0/6-31+G\* level of theory [34,35]. This study reveals that annulation and carbonylation of rNHCs results in decreases in thermodynamic and kinetic stabilities. Further, both annulation and carbonylation result in decrease in  $\sigma$ -donating ability but significant increase in  $\pi$ -accepting ability. The significant increase in  $\pi$ -acidity has been further corroborated by the calculated electrophilicity index values as well as  $^{31}\text{P}$  NMR chemical shift values of the corresponding rNHC-phosphinidene adducts.

**[1.7.2] Chapter 3: Effect of Ylide Substitution on the Stability and Electron Donation Ability of NHCs.**

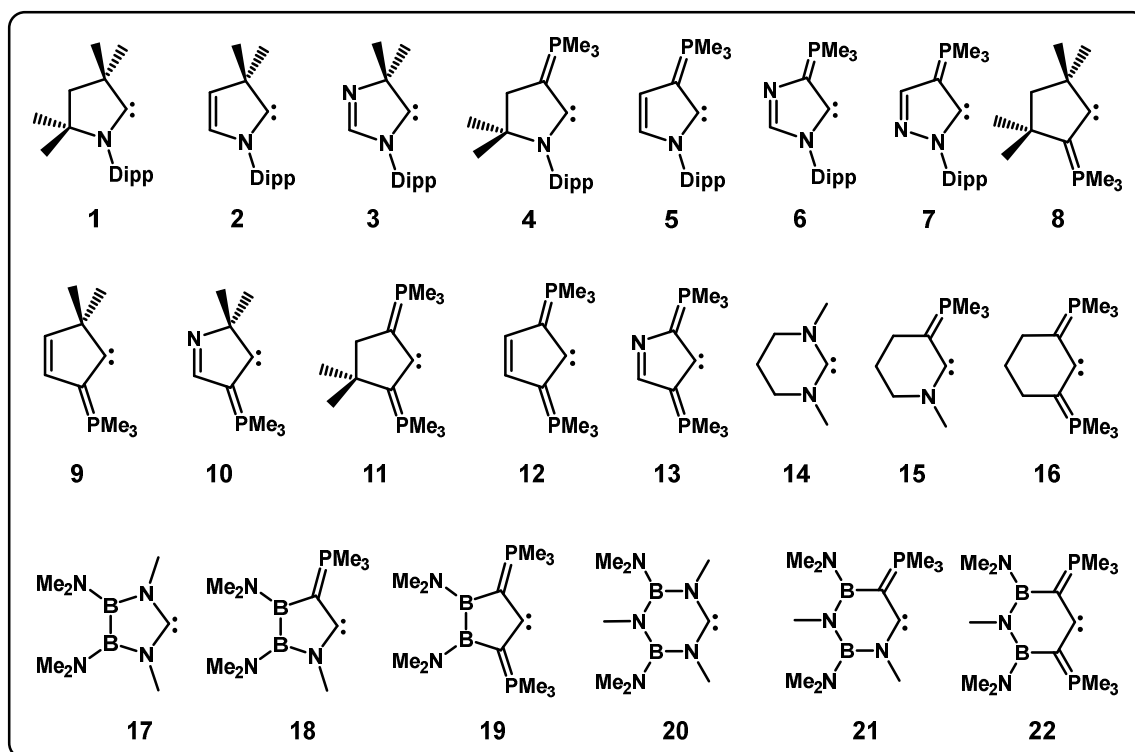
Following the isolation of the stable singlet NHC in 1991 [29], a number of their structural derivatives have been isolated which possess varying degree of ligand properties [36]. One of the interesting candidate of this family is cyclic(alkyl)(amino)carbene (CAAC), which possesses better  $\sigma$ -basicity and  $\pi$ -acidity than the normal NHCs [37]. Further, the seminal works of Kawashima and Fürstner in 2008 suggest that introduction of electron-donating phosphorus and sulfur ylide centers into the ring framework also leads to significant increase in  $\sigma$ -donation ability of cyclic carbenes [38].

This chapter contains two parts – (i) the first part of which deals with the effect of ylide substitution on the electron-donating ability and stability of a number of five- and six-membered cyclic carbenes and (ii) the second part deals with the theoretical studies aimed toward stabilization of five- and six-membered remote carbenes in their singlet ground states.

**[1.7.2.1] Moving Toward Ylide-Stabilized Carbenes.**

The electron-donating ability of a carbene ligand has a significant effect on the catalytic activity of the corresponding transition-metal complexes. Hence, the design and synthesis of carbene frameworks with enhanced electron-donating abilities may help to develop novel catalysts for various applications.

In this part, we have investigated the effect of ylide substitution at position  $\alpha$  with respect to the carbene carbon on the stability and  $\sigma$ -donating ability of a number of cyclic carbenes (Scheme 1.2) using PBE0/6-31+G\*, SDD level of theory [34,35,39]. The introduction of ylide centers into the ring framework dramatically enhances the  $\sigma$ -donating ability. Furthermore, for majority of the carbenes, ylide substitution leads to a significant increase in stability. The increase in  $\sigma$ -basicity in the ylide substituted ones has been further assessed by the calculation of carbonyl-stretching frequencies of the corresponding metal complexes, proton affinity values and the extent of gallium pyramidalization in the corresponding GaCl<sub>3</sub> adducts.

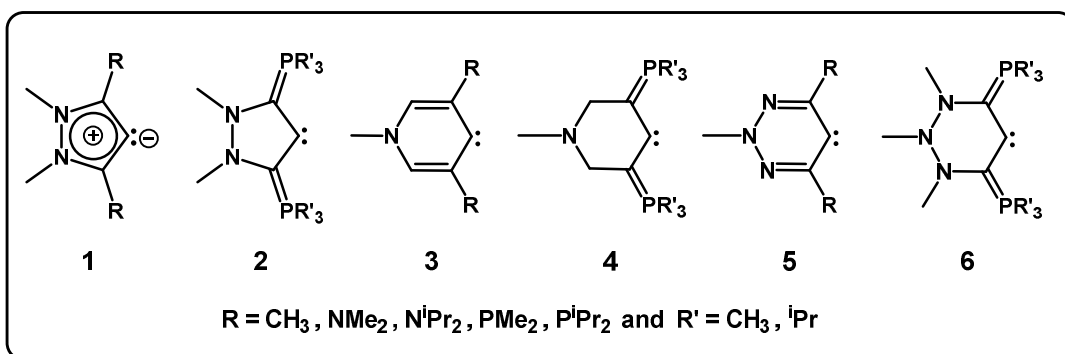


**Scheme 1.2:** Schematic representation of the range of carbenes considered in this study (Dipp: 2,6-diisopropylphenyl).

### [1.7.2.2] Theoretical Strategies Toward Stabilization of Singlet Remote *N*-Heterocyclic Carbenes.

Even though the remote NHCs (rNHCs) possess superior ligand properties in terms of both  $\sigma$ -donation and  $\pi$ -acceptance ability compared to the classical NHCs [32], so far no rNHCs have been isolated in their free state. In case of normal NHCs, the singlet state stability can be attributed to the effective  $\pi$  delocalization from the nitrogen lone pairs to the formally vacant p orbital at the carbene carbon. However, unlike in normal NHCs,  $\pi$  stabilization is not so effective in rNHCs resulting in lower singlet state stability.

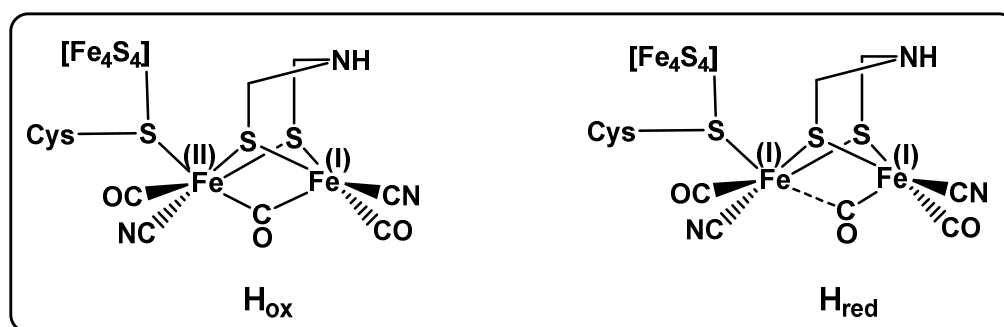
In this part, we present the results of theoretical studies aimed toward stabilization of five- and six-membered remote carbenes (Scheme 1.3) in their singlet ground states. The quantum-mechanical calculations carried out at PBE0/6-31+G\*, SDD [34,35,39] level of theory predict that the singlet states of ylide-substituted remote carbenes are significantly stable and comparable to those of experimentally known NHCs. Further, NICS [40] and QTAIM based bond magnetizability [26] calculations indicate the presence of cyclic electron delocalization in majority of the molecules.



**Scheme 1.3:** Schematic representation of the range of cyclic carbenes considered in this study.

### [1.7.3] Chapter 4: Carbene Driven Stabilization of the $\text{H}_{\text{red}}$ State of Biomimetic Model [FeFe]-Hydrogenase Complexes.

[FeFe]-hydrogenase is an enzyme which catalyzes the reversible activation of dihydrogen involving two key intermediates ( $\text{H}_{\text{ox}}$  and  $\text{H}_{\text{red}}$ , Scheme 1.4) [41]. One of the important structural features of both  $\text{H}_{\text{ox}}$  and  $\text{H}_{\text{red}}$  state of the native enzyme is the presence of an inverted square pyramidal geometry (or rotated geometry) at one of the iron center (distal) with a carbonyl group in bridging position between the two iron centers. The vacant site at the distal iron center is the probable site for coordination of  $\text{H}^+/\text{H}_2$  during reversible dihydrogen production [42]. Even though a number of model complexes for the  $\text{H}_{\text{ox}}$  state have been isolated with a rotated conformation, only a few model complexes for the  $\text{H}_{\text{red}}$  state were known with an inverted square pyramidal geometry at one of the iron center [43].

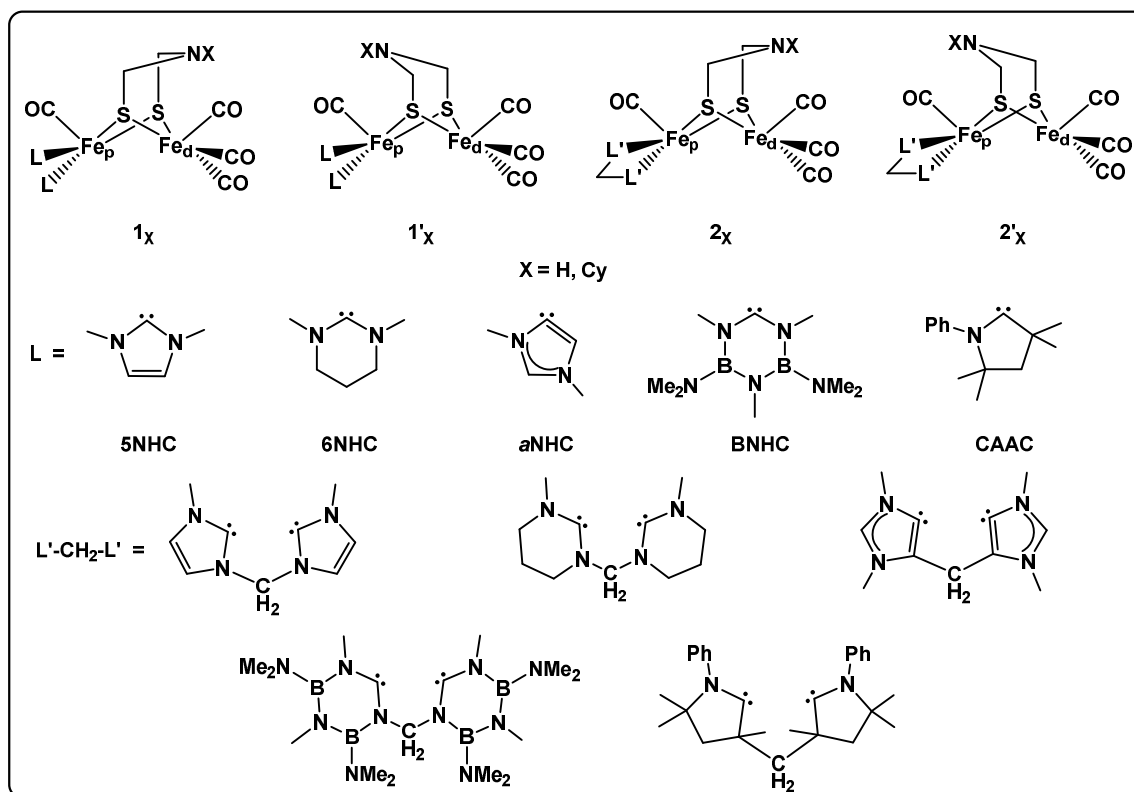


**Scheme 1.4:** Schematic representation of the active site structure of [FeFe]-hydrogenase.

In this chapter, we present our results of theoretical investigation toward stabilization of rotated structure in carbene substituted [FeFe]-hydrogenase model complexes (Scheme 1.5) carried out at BP86/Def2-SVP, Def2-TZVP(Fe) level of theory



[7,44]. Stabilization of fully rotated conformation at one of the iron center has been achieved for the reduced Fe(I)Fe(I) state in chelated CAAC substituted biomimetic hydrogenase model complex. This study indicates that the spatial orientation of the chelated NHCs at one of the iron center ( $\text{Fe}_p$ ) plays a major role in determining the geometry at the other ( $\text{Fe}_d$ ). We also made an attempt at explaining the electronic origin behind the favorability of rotated vs unrotated structure in asymmetrically substituted chelated vs monodentate NHC complexes.

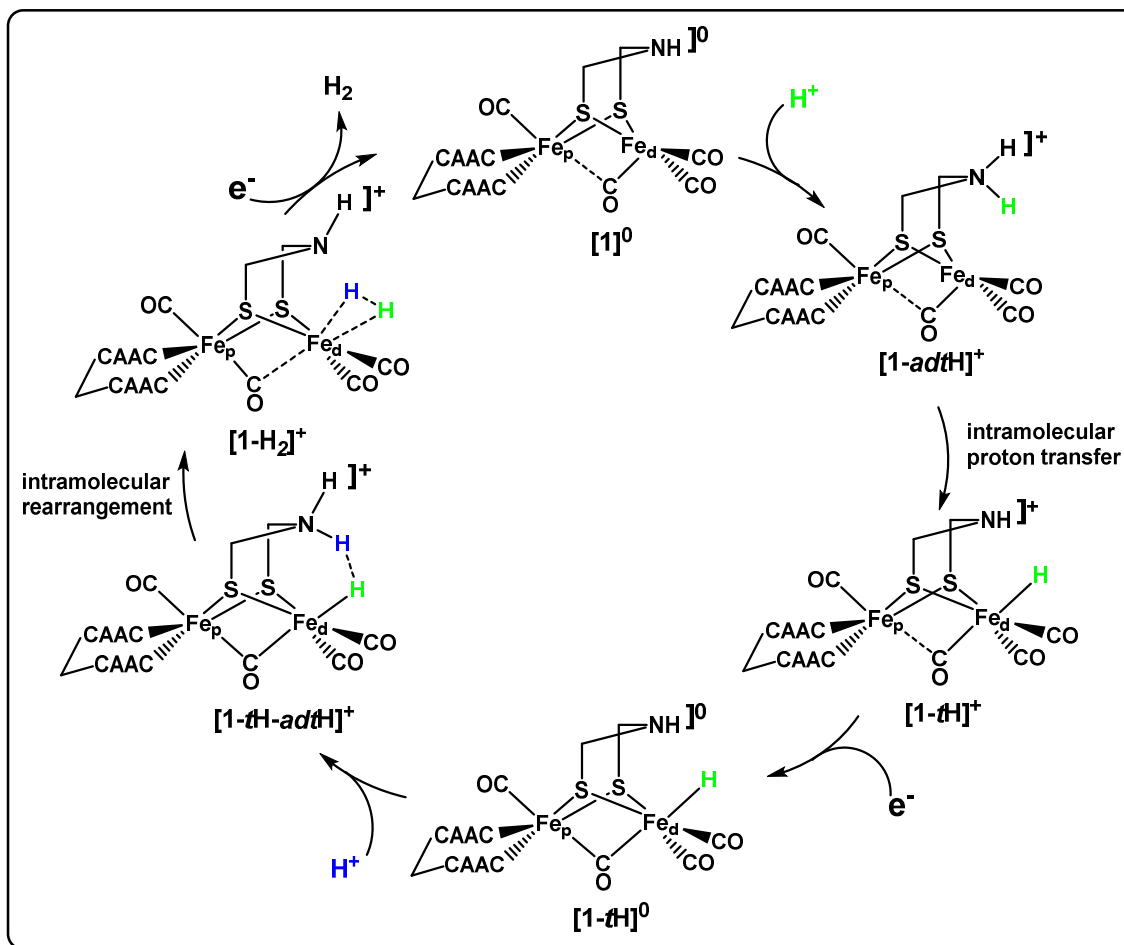


**Scheme 1.5:** Schematic representation of the molecules considered in the present study (X= H/Cyclohexyl).

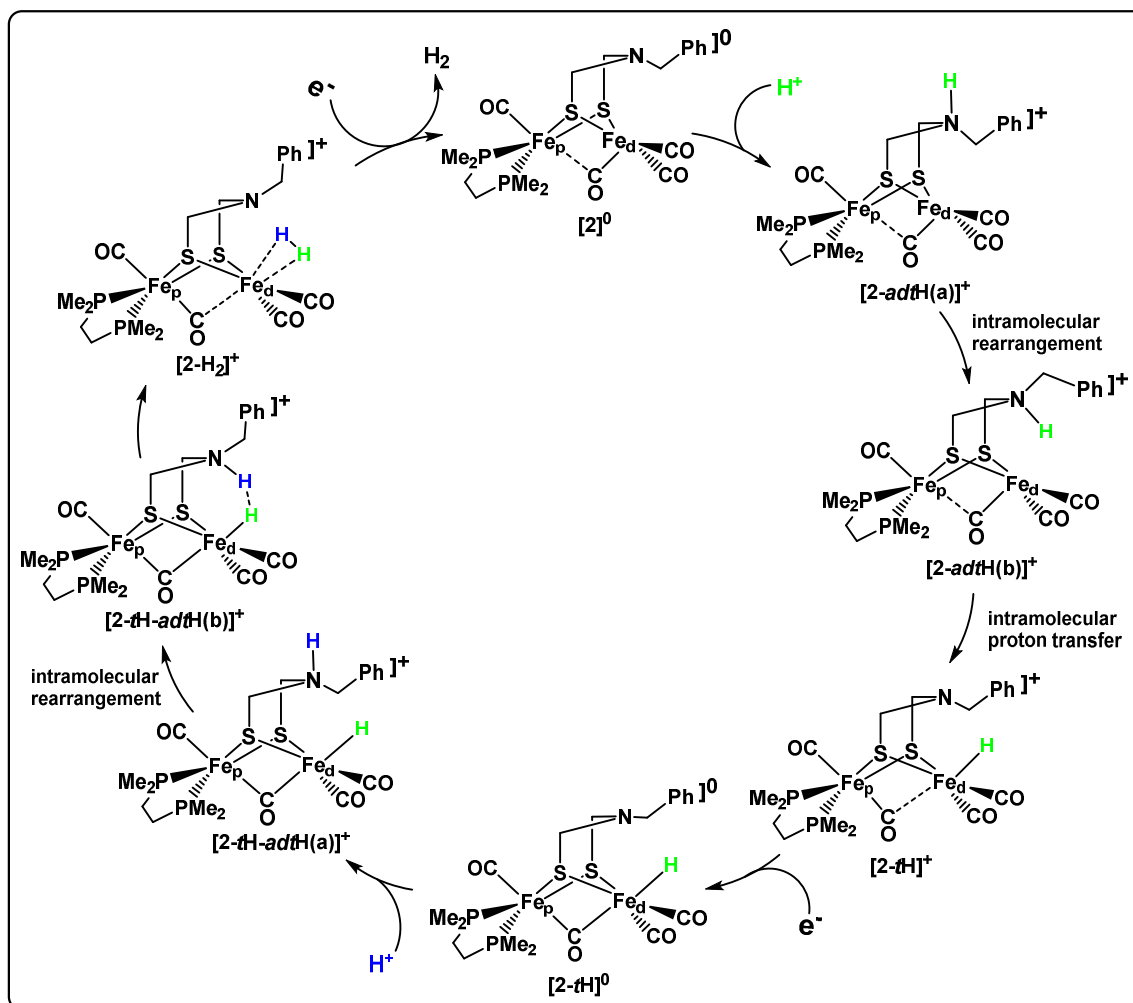
#### [1.7.4] Chapter 5: Can Carbene Decorated [FeFe]-Hydrogenase Model Complexes Catalytically Produce Dihydrogen? An Insight from Theory.

In this chapter, we have studied the mechanistic details of catalytic production of dihydrogen using bio-inspired [FeFe]-hydrogenase model complexes which possess rotated conformation at one of the iron centers ( $[1]^0$  and  $[2]^0$ , Scheme 1.6 and 1.7). The catalytic evolution of  $\text{H}_2$  is found to be highly favourable using both the complexes as evident from high exergonicity of the overall reaction as well as very shallow activation energy barrier for the transition states involved. The computed reduction potential values

are found to be less negative compared to those reported earlier for experimentally known system.



**Scheme 1.6:** Schematic representation of the catalytic cycle of H<sub>2</sub> production catalyzed by  $[1]^0$ .



**Scheme 1.7:** Schematic representation of the catalytic cycle of H<sub>2</sub> production catalyzed by  $[2]^0$ .

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