Chapter 2

Theoretical Background and Methods

2.1 Introduction

Theoretical chemistry uses mathematical methods which are related to the physics fundamental laws and study the chemical relevance. By the theoretical chemistry, we can calculate the many properties such as a stable geometrical arrangement of the nuclei, their relative energies, rate, polarizability, dipole moment etc. In earlier times theoretical chemistry was not a vast area but due to the increase of technology, theoretical chemistry has become a very broad area nowadays. It deals with many areas of chemistry such as atmospheric, physical, inorganic, organic, bioinorganic chemistry. Along with chemistry it is also used in physical, mathematical, biological, and computer science, etc. and provides an idea to solve electronic properties and provide connections between all these branches of science.

Quantum chemistry deals, fundamentally, with the motion of electrons under the influence of the electromagnetic force exerted by nuclear charges. To understand the electronic structure, and rate of reaction quantum chemistry is used, which is based on the Schrödinger equation (time-independent and time-dependent). In the present thesis, ground-state chemical reactions have been studied, that's why it is sufficient to use the time-independent Schrödinger equation.[3,4] However, one-electron system equations can be solved by it, but it is very complicated for the many-electron system. For which many approximations are taken. It is extensively used in the design of new drugs and materials. It can be also used to find out the molecular geometry, energies of molecules, transition states, chemical reactivity, IR, UV, and NMR spectra. It can also be used to study the interaction of a substrate with an enzyme and the physical properties of substances etc. The development of DFT gives a very big achievement in computational chemistry. DFT is based mainly on electron density. DFT method has been used for modeling electronic structure and mechanism in this thesis.

Quantum mechanics is mainly divided into three parts

1. Hartree-Fock Theory

2. Semi-emipirical methods

3. Density Functional Theory

2.2 Hartree-Fock Theory (HF)

The most important and primary function of computational methods is to obtain the wave function of the system which gives all the information about the quantum mechanical behavior of the system. The main paradigm is to find out the energy of the molecular system.[5-8]

The time-independent Schrödinger equation[9] is shown in equation 2.1.

$$\widehat{H}\psi \ = \ E\psi \tag{2.1}$$

Where Ψ is wave function associated with the system, E is the energy eigenvalue of Hamiltonian operator contains kinetic energy and potential energy terms.

Schrödinger's equation cannot be solved exactly for more than one electron. Therefore, there are several approximations for solving the Schrödinger equation for molecules with more than one electron system. First, an approximation is a Born-Oppenheimer approximation, it considers that the mass of nuclei is very large as compared to electron, thus we may consider that nuclei are stationary and it also neglects the relativistic effects, and they reduce the many-electron problem to one-electron problem. Then, the Schrödinger equation for the electronic motion is given by

$$\widehat{H}_{elect}\psi_{elect} \ = \ E_{elect}\psi_{elect} \tag{2.2}$$

Where, $\widehat{H}_{elect}$ is the pure electronic Hamiltonian

$$\widehat{H}_{elect} = -\sum_{i=1}^{n} \frac{h^2}{4\pi m_e} \nabla_i^2 - \frac{1}{4\pi\varepsilon_\circ}\left(\sum_{i=1}^{n}\sum_{\alpha=1}^{M} \frac{Z_\alpha e^2}{r_{i\alpha}} - \sum_{i=1}^{n}\sum_{j>i}^{N} \frac{e^2}{r_{ij}}\right) \qquad (2.3)$$

Where m_e is the mass of each electron and M is the number of nuclei. The α-th nucleus has mass M_α and charges $Z_{\alpha e}$ where e is the electronic charge. Electronic coordinates are written as r_i's. Unfortunately, the Born-Oppenheimer approximation is not sufficient to solve the Schrödinger equation for many-electron systems. The basic wave function method is known as Hartree-Fock method, which is based upon an independent molecular orbital model. In the HF method, each electron is described by an orbital; total wave function is given by the product of orbitals, where wave function is considered by the approximation. The wave function is solved by the time-independent Schrödinger equation and the relativistic motion is not taken into consideration.

According to it Schrödinger equation of a molecule may be divided into electronic and nuclear energy. These quantum chemical models differ in the nature of approximations employed and spanned over a wide range both in terms of their capability and reliability. It is an *ab initio* type calculation, in which columbic electron-electron repulsion is taken into account, and it gives the average effect, it does not include explicit repulsions. This is a variational calculation; in which calculated average energy is always equal to or greater than the exact value. In many-electron system Schrödinger equation is broken down in the single electron approximation, and the wave function is the linear combination of atomic orbitals (Gaussian type Orbital (GTO)). The limitation of the approximation is that it does not take into account the corre Hartree-Fock uses single Slater type determinant.[10] Single Slater determinant gives the accurate description of the system. HF considers the interaction of each electron with mean-field of electrons, instead of considering the individual electron-electron interaction separately. The energy calculated with HF is too high, and increase in energy due to this error is referred correlation energy i.e. it calculates the probability of finding an

electron around an atom by taking the distance from the nucleus which does not take into account the distance of an electron from other electrons. The HF energy after adding correlational energy will give the exact solution to the Schrödinger equation. By increasing the quality of basis sets, the calculated energy can approach the exact solution. HF theory only takes into account the average electron-electron interaction and neglects the electron correlation. Due to which it lacks a certain amount of electronic energy. This missing energy only represents a small percentage of total energy while it is essential to solve the chemical problems and to evaluate the relative energy.
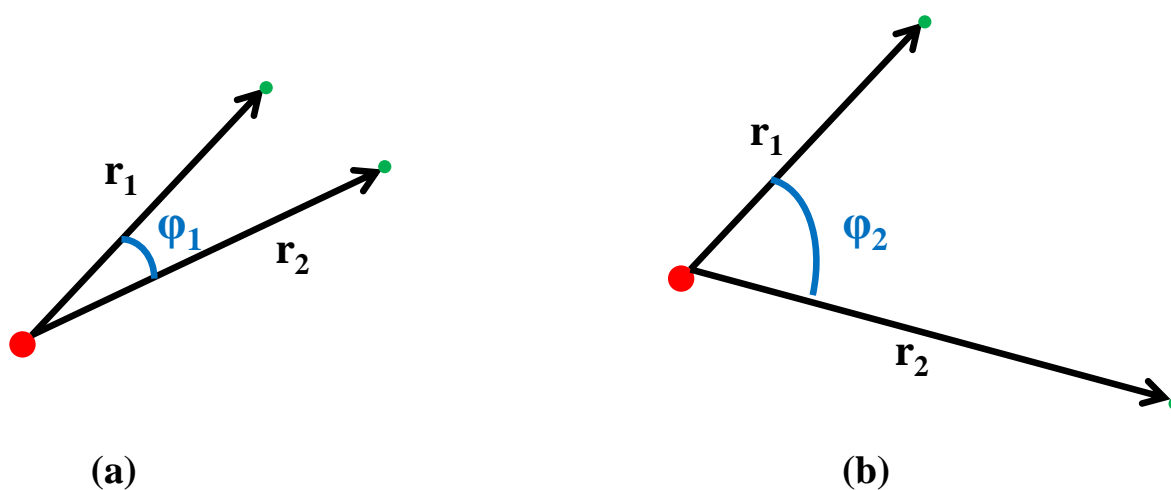

(a)   **(b)**

Figure 2.1. Two different arrangements of electrons in atom around the nucleus have same probability within HF theory, but not in correlated calculations.

To improve the accuracy beyond the HF method, explicit electronic correlations to be include. To include the electron correlation, multi-determinant wave function is used which is beyond Hartree-Fock. Some of these are Möller-Plesset perturbation methods (e.g. MP2 and MP4), configuration interaction method (e.g. CISD), multi-configurational self-consistent field (MCSCF), configurational interaction (CI), and coupled-cluster methods (e.g. CCSD (T)). These methods are multi determinants and optimize both their orbitals and coefficients. NEVPT2 (N-electron valence state perturbation theory) is the multireference method using perturbation theory, it improves the results significantly. Computed molecular geometry and

energies are more accurate that includes correlation. However, these theories require a large computational facility and are expensive. Thus, it can be applied to small systems, while for the large system we have to use alternative methods. An alternative to the wave function-based method is density functional theory (DFT), which is used for understanding chemical problems.

2.3 Semi-empirical Method

Semi-empirical calculations are performed by taking the structure of the HF i.e. Hamiltonian and wave function, where some information is approximated or completely omitted. The core electrons are not included in the calculation. Parameterizations are used to predict the omitted parameters and are calculated either by experiments or by *ab initio* calculations. For example, Hückel, Pariser-Parr-Pople (PPP), complete neglect of differential overlap (CNDO), modified intermediate neglect of differential overlap (MINDO), Intermediate neglect of differential overlap (INDO), and Austin Model 1 (AM1). These methods are faster than the *ab initio* calculations. The disadvantage of these methods is that these results depend upon the parameterization, if the computed molecule is similar to that is used to parameterize the method then the results are good otherwise not.

2.4 Density Functional Theory (DFT)

According to DFT, energy is calculated by the electron density, not by the wave function. Here, "*electronic energy is functional of electron density which is a function of space and time*".[11-13] DFT theory was developed by the theorem proposed by Hohenberg and Kohn. In this theory, the determinant is formed by the electron density. DFT is classified into many classes that include the electron exchange, not the correlation. Density functional theory is

based on electron density instead of the wave function. DFT is based on two Hohenberg-Kohn theorem.[14,15]

The first, Hohenberg-Kohn theorem, states that "*any ground state property of a molecule is a functional of the ground-state electron density function*".

$$E_o = F[\rho_o] = E[\rho_o] \tag{2.4}$$

This theorem assures that many molecular properties can be calculated from the electron density, and approximate functional will give at least approximate answers. The second Hohenberg-Kohn theorem is the DFT analog of the wave function variation theorem that has connection with the *ab initio* method. It states that "*any trial electron density function will give energy higher than (or equal to, if it were exactly the true electron density function) the true ground state energy*".

$$E_v[\rho_t] \geq E_o[\rho_o] \tag{2.5}$$

DFT methods give more accurate structures and vibrational energies for the transition metals than the Hartree-Fock methods and their results are similar to the post-HF method. DFT calculations are computationally less expensive and become the routine choice of method for transition metal compounds.[16-23] The approximate functional employed by current DFT methods partition the electronic energy into several terms:

$$E = E_T + E_V + E_J + E_{Exc} \tag{2.6}$$

Where, E_T = kinetic energy arising from the motion of electrons,

E_V = potential energy of the nuclear-electron attraction and the repulsion between

pairs of nuclei

E_J = Coulomb self-interaction of electron-electron

E_{Exc} = exchange-correlation energy term

2.4.1 Exchange correlation functional (E_{xc})

The E_{xc} function not only defines the difference in kinetic energy of an interacting and non-interacting system but also deals with the difference between classical and quantum mechanical electron repulsion.

$$E_{xc} = E_x + E_c \tag{2.7}$$

For the total energy calculation there is a requirement to make the approximation for the exchange-correlation energy, and the DFT method's accuracy depend upon how well the approximations have been made. Beyond, the pure electrostatic interactions exchange-correlation potential describes Pauli's principle effects coulomb potential.

Classification of density functional theory has been proposed and some of them are discussed here.

(a) Local density approximation (LDA)

Local density approximation (LDA) is applicable on uniform electron gas i.e. electron density varies very slowly with the position.[24,25] In LDA, functional depends on the electron density at each point in space. The term local is used because at any point only the conditions at that point are considered, while in nonlocal methods at each point a gradient, which considers the region a bit beyond the point is used. These calculations are performed for the study of band structure; its results are not good for the calculation of molecular structure where errors of both qualitative and quantitative results are incorporated. The exchange-correlation energy[15] is written as;

$$E_{xc}^{LD} = \int d^3 r n(r) E_{xc}^{unif} n(r) \tag{2.8}$$

Where, $E_{xc}^{unif} n(r)$ = exchange-correlation energy of uniform electron gas

Better results than LDA can be obtained by elaborating LDA, that alpha (α) and beta (β) electrons have different orbitals say, $\psi_\alpha = \psi_\beta$, by which they have different electron densities ρ^α and ρ^β. This "unrestricted" LDA method is known as local spin density approximation. The advantage of LSDA is that it can handle systems like radicals, which are having one or more unpaired electrons, and the systems in which electrons are going to get unpaired. In LSD approximation, the exchange functional is given by

$$E_{xc}^{LSD}[n_\uparrow][n_\downarrow] = \int d^3r \; n(r) E_{xc}^{unif}(n_\uparrow(r), n_\downarrow(r)) \tag{2.9}$$

Where, $E_{xc}^{unif}(n_\uparrow(r), n_\downarrow(r))$ is exchange-correlation energy of each particle of a uniform electron gas with spin densities $n_\uparrow(r)$, and $n_\downarrow(r)$. Ground state properties such as lattice constant, bulk, etc. are described in LDA, and the dielectric constant is 10-40 % overestimated in LDA as compared to the experiment. This overestimation is due to the neglect of a polarization-dependent exchange-correlation in LDA as compared to LSDA. It can be improved by including the gradient of density in functional. The generalized gradient approximation (GGA) is an example of this type of approach.

(b) Generalized-gradient approximation (GGA)

The electron density in an atom or molecule varies greatly from place to place, so it is not surprising that the uniform electron gas model has serious shortcomings. It assumes non-uniform electron gas. It takes the exchange and correlation energy. These depend not only on electron density but also depend on its gradient (first derivatives of density with respect to position). These functional are called *gradient corrected,* or said to use the *generalized gradient approximation* (GGA). They are also called *nonlocal* functional or "*semi local*". GGA functional proposed for the correlation energy. The general formula for GGA functional is:

$$E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3 r n(r) E_{xc}^{GGA}(n_\uparrow, n_\downarrow, \Delta n_\uparrow, \Delta n_\downarrow) \tag{2.10}$$

One popular functional was proposed by A.D. Becke (B or B88)[26]

$$\varepsilon_x^{B88} = \varepsilon_x^{LDA} + \Delta \varepsilon_x^{B88}$$

$$\varepsilon_x^{B88} = -\beta \rho^{1/3} \frac{x^2}{1 + 6\beta x \sinh^{-1} x}$$

$$x = \frac{|\nabla \rho|}{\rho^{4/3}}$$

One popular GGA functional is *Lee*, *Yang,* and *Parr* (LYP),[27,28] the LYP functional does not include parallel spin correlation when all the spins are aligned (e.g. the LYP correlation energy for ^{3}He is zero). The LYP correlation functional is often combined with the B88 or OPTX exchange functional to produce the BLYP and OLYP acronyms. DFT calculations with functional incorporating gradient corrections, and the HF exchange term (hybrid functional), can be speeded up with only a little loss in accuracy by a so-called perturbation method.

(c) Meta generalized-gradient approximation (MGGA)

It is an extension of GGA methods and it allows the exchange and correlation functional to depend on higher-order derivatives of the electron density. Inclusion of either the Laplacian or orbital kinetic energy density as a variable leads to the so-called *meta-GGA* functionals[29-31] Calculation of the orbital kinetic energy density is numerically more stable than a calculation of the Laplacian of the density. Results have more accuracy than the earlier approximations. The normal form of the meta-GGA functional is

$$E_{xc}^{mGGA}[n_\uparrow, n_\downarrow] = \int d^3 r n(r) E_{xc}^{mGGA}(n_\uparrow, n_\downarrow, \Delta n_\uparrow, \Delta n_\downarrow, \Delta_{n_\uparrow}^2, \Delta_{n_\downarrow}^2, \tau_\uparrow, \tau_\downarrow) \tag{2.11}$$

The most popular GGA functionals are TPSSh, M06-L, etc.

(d) Hybrid density functional methods

Hybrid Density Functional methods are also known as the *Adiabatic Connection Model* (ACM).[32-34] Correlation energy may similarly be taken as the LSDA formula plus a gradient correction term. There is an exact connection between the non-interacting density functional to the fully interacting many-body systems which allow for calculating the exact exchange-correlation functional. It is the combination of Hartree-Fock exchange-correlation and density functional. This generally has a linear combination of HF exact exchange functional.

$$E_{xc} = (1-a)_{Ex}^{DFT} + aE_x^{HF}$$ (2.12)

Models that include exact exchange are often denoted as hybrid methods and Becker 3 parameter functional (B3) methods are examples of such hybrid models, B3LYP is one of the most widely employed hybrid functional. It is a combination of the three parameters such as exchange-correlation, LSDA and gradient corrected term. It was developed by Becke in 1993, modified by Stevens *et al.* in 1994 by the introduction of correlation-energy functional LYP 1988. It is used for calculating the atomization energies, ionization potentials, proton affinities, and total atomic energies of small molecules. For improving the exchange-correlation functional a portion of HF theory is added to it, the resulting functional is called hybrid functional. It is given by

$$E_{XC}^{B3LYP} = (1-a_o-a_x)E_x^{LSDA} + a_oE_x^{HF} + a_xE_x^{B88} + (1-a_c)E_c^{VWN} + a_cE_c^{LYP}$$ (2.13)

Where, E_x^{LSDA} is 'pure DFT' LSDA non-gradient-corrected exchange functional, E_x^{HF} is the KS-orbital-based HF exchange energy functional, E_x^{B88} is the Becke exchange functional, E_c^{VWN} is the Vosko, Wilk, Nusair function, E_c^{LYP} is the LYP correlation functional. The parameters a_o, a_x and a_c are those that give the best fit of the calculated energy to molecular atomization energies. The general form of the functional is given below,

$$E_{XC}^{HF} = E_{XC}^{LSDA} + 0.2(E_X^{HF} - E_X^{LSDA}) + 0.72\Delta E_X^{B88} + 0.81\Delta E_c^{PW91}$$ (2.14)

Here, ΔE_X^{B88} and ΔE_C^{PW91} are the GGA corrections that are widely used to LSDA exchange and correlation energies respectively.[35-36]

(e) Density functional theory including dispersion corrections

At the fifth level of Jacob's ladder classification, the full information of the KS orbitals is employed, i.e. not only the occupied but also the virtual orbitals are included. The formalism here becomes similar to those used in the random phase approximation, but a little work has appeared on such methods. Inclusion of the virtual orbitals is expected to significantly improve, for example, dispersion (such as Vander Waals) interactions, which is a significant problem for several functionals. The optimized effective potential (OEP) method can be considered in this category.[4]

By using DFT, many properties such as spectroscopic including IR, UV, and NMR spectra can be studied, along with these properties such as dipole moments, bond orders, charges, ionization energies, electron affinity, electronegativity, harder and softer properties can be studied. DFT functionals are not capable of describing the weak forces of attraction like Vander Waal forces and non-covalent interactions. B3LYP functional is named as B3LYP-D/D2/D3 functional after the addition of dispersion correction term.[37-39] Some functionals like M06[40] suite and B97D[41] are present in which dispersion correction term is already included in their functional form. To predict the performance of a functional in DFT, one must have to try on a variety of molecules and properties to assess its performance. DFT is mainly the ground state theory; researchers are working to extend it to the excited state.

For this, an alternative approach is used i.e. time-dependent Schrodinger equation to calculate the absorption of energy from light by calculating effect of the time-dependent electric field on the molecule.
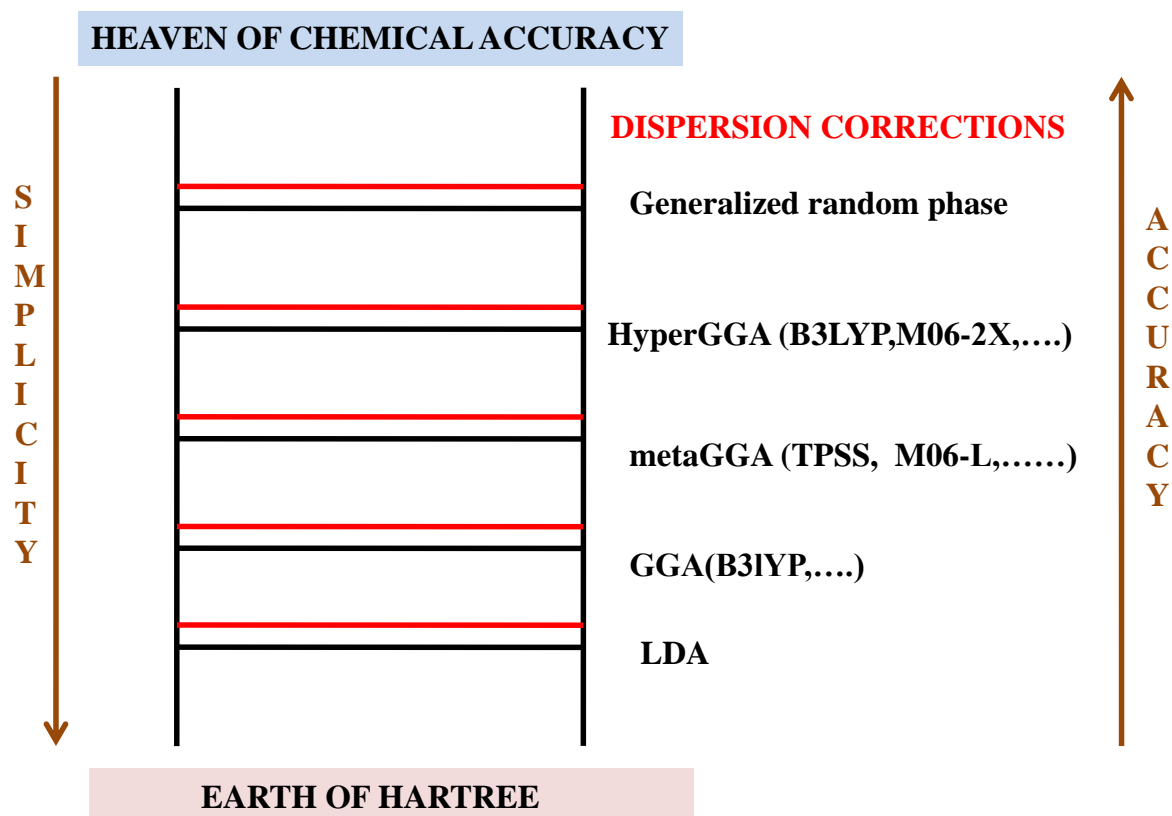
Figure 2.2. Classification of XC functionals by Jacob's ladder.

It is an alternative development of time-dependent quantum mechanics, in which density is the fundamental variable instead of many-body wave function. Time-dependent density is calculated by solving the non-interacting Schrodinger equation.[46]

Theorem of TDDFT confirms the one-to-one correspondence between electronic density $n(r,t)$ and the external (time-dependent) potential, V_{ext} (r,t), for many-body systems evolving from a fixed initial state.[46] First time, TDDFT calculation was performed by Ando to predict the inter sub-band transition in heterostructure of semiconductor.[47] Zangwill and Soven[48] performed the first calculations for finite systems.

For, the more accurate TDDFT results, Casida and Salahub stated that these two criteria should follow: (i) Excited energy should be smaller as compared to molecular ionization potential. (ii) Excitations should not be in orbitals having positive KS eigenvalues. For many

absorptions results, organosulphur compounds B3LYP, TDDFT and INDO/S results were compared by the Fabian.[49] It was found that the performance of TDDFT is good.

2.5 Basis Sets

"Basis set is a group of mathematical functions used to describe the shape of the orbitals in a molecule".[50] Molecular orbitals are the linear combination of basis function and angular function. It gives a mathematical description of atomic orbitals. There are two types of atomic orbitals; one is Slater type and the other is Gaussian type orbital. It was Slater who proposed atomic orbitals first time, which correspond to a set of functions in which distance from the nuclei decays exponentially $(e^{-\xi r})$.[51] The expression for the Slater type orbital is

$$G_{\xi,n,l,m}(r,\theta,\varphi) = N Y_{l,m}(\theta,\varphi) r^{n-1} e^{-\xi r} \tag{2.15}$$

Slater-type orbitals are used for the atoms having many electrons whose analytical solution is difficult and computational studies are expensive. Alternative for the slater type orbital is the linear combination of Gaussian type orbitals (GTO). In Gaussian type orbitals the distance from nuclei decay as $e^{-\xi r^2}$.

$$G_{\xi,n,l,m}(r,\theta,\varphi) = N Y_{l,m}(\theta,\varphi) r^{2n-2-l} e^{-\xi r^2} \tag{2.16}$$

The exact solution of the Schrodinger equation for the hydrogen atom is the Slater type orbital. GTO requires more primitive than the STO to describe the wave function. However, the numeric integral over GTO can be computed analytically much faster than the STO that's why a given accuracy can be obtained quickly using the GTO.
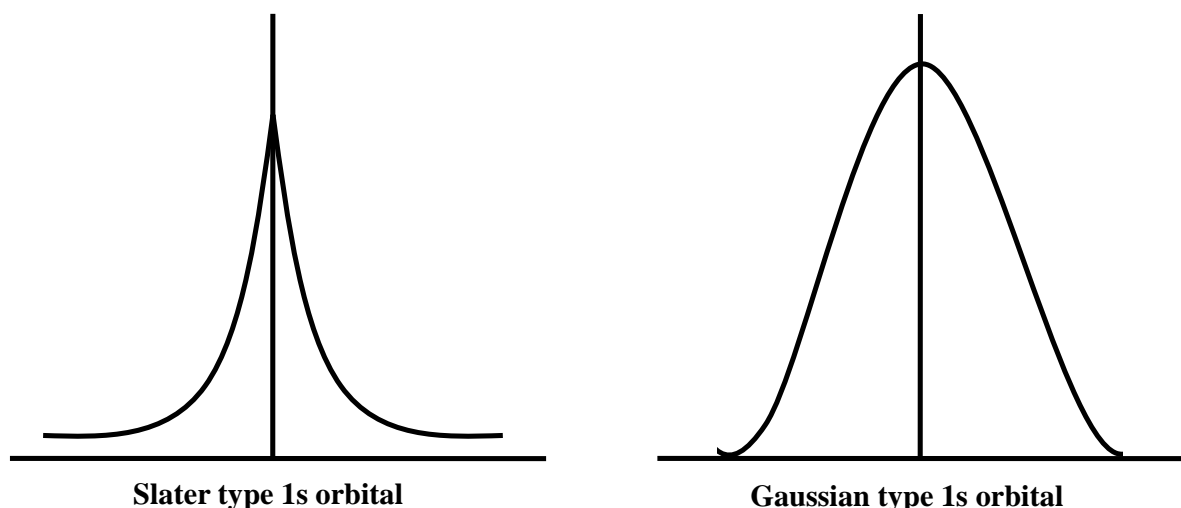
Figure 2.3. Slater type orbital (STO) and Gaussian type orbital (GTO).

The normalized Gaussian type orbital in Cartesian coordinates is given by

$$\varphi(x, y, z; i, j, k) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left[\frac{(8\alpha)^{i+j+k} i! j! k!}{(2i)!(2j)!(2k)!}\right]^{1/2} x^i y^j z^k e^{-\alpha(x^2+y^2+z^2)} \tag{2.17}$$

Where,

Exponent α, and i, j, and k = non-negative integer and these define the nature of orbital in a Cartesian type.

If all the three indices (i, j, and k) are zero, then the GTO has spherical symmetry is called an s-type GTO. When only one index (i, j, k) have value one, then it has axial symmetry about a single Cartesian axis is called p-type GTO. When the sum of i, j, and k is one, then it is called p-type GTOs have three functions named as p_x, p_y, and p_z orbitals and when the sum of indices is equal to two, then it is d-type GTO. A complication arises for basic functions with d orbitals or higher symmetry orbitals. Five d real orbitals are xy, xz, yz, x^2-y^2, and d_z^2, where z^2 is $2z^2$-x^2-y^2. For the fast integral, evaluation is to use the six Cartesian orbitals, which are xy, xz, yz, x^2, y^2, and z^2. These six orbitals are equivalent to 5 pure d orbitals and one additional spherically symmetric function x^2+y^2+z^2. Calculations using the $6d$ orbitals have lower energy than the calculations performed with $5d$ orbitals because of the additional

function. Some *ab intio* programs have the option to use 5*d* (pure-*d*) or 6*d* (Cartesian). Similarly, with *f* orbital 7*f* (pure-*f*) and 10*f* (Cartesian).

Choosing a standard GTO basis set means that the wave function is defined by a finite number of functions. This created the approximation in calculations. To describe the wave function exactly infinite numbers of GTO functions are needed. Differences in results due to the quality of the basis set *vs.* another are known as basis set effects. To avoid the basis set effects, some high-accuracy work is done with a numeric basis set. Cubic spline set is an example of such a basis set. The choice of basis set affects the CPU time required to perform the calculation. The amount of CPU time for Hartree-Fock calculations scales N^4. For example, we have to twice the calculation then it will take the time 2^4 (16) times longer.

2.5.1 Classification of basis sets

Minimal basis set:

When the minimum number of basis functions are used to represent each orbital in an atom, is known as a minimal basis set, for example, STO-G, STO-6G, etc.[52-54]

e.g. One s function for H (1s); and 5 basis function for N (1s, 2s, $2p_x$, $2p_y$, $2p_z$).

Double/triple zeta basis set:

Doubling all the basis functions gives rise to the double zeta function. e.g: two s functions for H (1s and 1s′), and 10 basis functions for N (1s, 1s′, 2s, 2s′, $2p_x$, $2p_y$, $2p_z$, $2p_{x'}$, $2p_{y'}$ and $2p_{z'}$)

 Split valence basis set:

As the separate basis functions are used singly for core and multiple for valence orbital it gives split valence basis set[55] and these can be Valence Double/Triple/Quadruple Zeta function. When the double basis function is used for valence orbital and then it is the valence

double zeta (VDZ) when the triple basis function is used then it gives valence triple zeta (VTZ) basis set.

N = (1s, 2s, 2s′, $2p_x$, $2p_y$, $2p_z$, $2p_{x'}$, $2p_{y'}$ and $2p_{z'}$) Valence double zeta

N = (1s, 2s, 2s′, 3s', $2p_x$, $2p_y$, $2p_z$, $2p_{x'}$, $2p_{y'}$ and $2p_{z'}$, $3p_{x''}$, $3p_{y''}$, $3p_{z''}$) Valence triple zeta

Split valence basis set is represented as *k-nlmG* in **Pople notation**.

Where,

k = number of primitive Gaussians (PGTOs)

nlm = number of Gaussian functions for the valence orbitals that are split into the PGTOs for a specific basis set

Two values (*nl*) indicate double split valence while three values (*nlm*) indicate a triple split valence basis. e.g. 6-31G, 6-311G
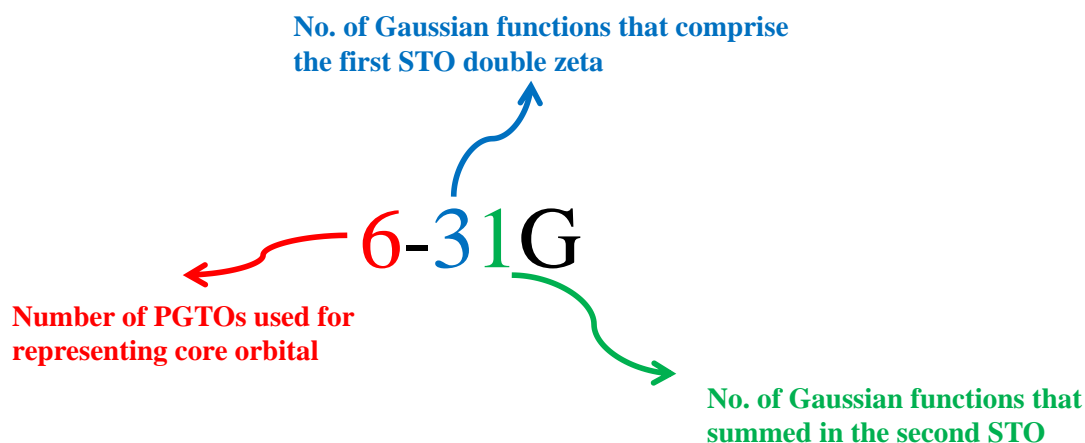
No. of Gaussian functions that comprise the first STO double zeta

6-31G

Number of PGTOs used for representing core orbital

No. of Gaussian functions that summed in the second STO

Figure 2.4. Basis set notation.

Polarization/diffusion basis set:

When polarization (angular momentum) function included then it is known as the polarization basis set.[56] It is denoted by an asterisk (*, **). A single asterisk (*) denotes that the *d* polarization function has been added to each atom except hydrogen and helium atoms. Two asterisks (**), indicates that a polarization *p* basis function is also added to hydrogen and helium atom. Polarization functions are represented after G with a separate designation for heavy and hydrogen atoms. The 6-31G* basis is identical to 6-31G (*d*), and 6-31G** is identical to 6-31G (*d*, *p*). In general, to polarize a basis function with angular momentum (*l*), mix it with the functions of angular momentum (*l*+1), e.g. polarized basis set adds *d* functions to a carbon atom and *f* function to transition metals.[14] These are functions of higher angular momentum and help to describe anisotropic charge distributions around the nuclei. Polarized functions are important for accurate description of bonding between atoms because the presence of other atoms distorts the environment of electrons and removes its spherical symmetry. These give more accurate computed geometries and vibrational frequencies. The basis set 3-21* shows the exceptionality that the *d* functions are added to 2nd row atoms. To indicate this difference, this basis set is given the notation 3-21(*).

Diffuse functions are added when there is electron density found far from the nuclei.[57] It is denoted by a plus sign (+). Single '+' denotes that diffuse function is added to all atoms except hydrogen and helium. While the Double ('++') indicates that diffuse function is also added to atoms along with hydrogen and helium. Diffuse functions are represented before the G, for example, 6-31++G. Diffuse functions are used for anions and for describing interactions at long distances, such as Vander Waals interactions. These basis functions are essential for the description of weak interactions such as hydrogen bonding and molecules having lone pairs. Diffuse functions change the relative energies of the various geometries associated with these systems.

Many basis sets are identified by the author's surname such as Huzinaga, Dunning, and Duijneveldt basis set, and along with surname, the number of primitive is also used such as D95 is the basis set created by Dunning with nine s primitives and 5p primitives. Semi-empirical methods are formulated to neglect the core electrons while the *ab initio* method represents. The elements in the lower part of the periodic table have a large number of core electrons, and core electrons are not involved in chemical transformation, but it is necessary to use a large number of basis functions to expand it, otherwise, the valence orbitals will not be described properly. There is the lower part of periodic table relativistic effects are also important. Further, to reduce the heavy computation necessity for the heavy elements. This is done by modeling the core electrons by a suitable function and treating the valence electrons explicitly.

Effective core potential

By replacing core electrons and their basis functions in the wave function with a potential term in Hamiltonian. This is called core potential, effective core potentials (ECP), or the relativistic effective core potentials (RECP) in the chemical community, while in the physics community it is known as pseudopotential. [58-60] Core potentials must be used along with a valence basis set that was created to accompany them. To reduce the computation time, relativistic mass defect and spin coupling term are significant near the nuclei of heavy atoms. To generate the pseudopotential, and LSD atomic calculation was performed using the method of Troullier and Martins. For example, LanL1MB and LanL2DZ (Los Alamos National Laboratory 2 Double-Zeta).

A limitation with the pseudopotential method is that it does not describe the properties which depend directly on core electrons such as X-ray photoelectron spectroscopy and the electron density near to nucleus i.e. NMR shielding and coupling constants. One common thing of

pseudopotential is that the parameters depend on the employed method, i.e. potential derived e.g. Local spin density approximation (LSDA) functional is different from that derived from a generalized gradient functional such as (PBE) Perdew-Burke-Ernzerh. In practice, the difference is small and pseudopotential optimized for one functional is used with other functional without re-optimization.

2.5.2 Basis set superposition errors

Most of the basis set's molecular applications are centered on the nuclei. A complete basis set cannot be used in practice, M_{basis}^4 increases computational effort limits for practical calculations to hundreds or a few thousand basis functions at best. The absolute errors in energy from basis set are quite large, may be several au or kJ/mol. There is usually interest in relative energies; to make errors as constant as possible. Thus, it is important to select a "balanced" basis set. Same basis set must be used for comparing energies, for example, for comparing energies of two isomers, 6-31G basis set is used for one, and DH basis set for other isomer is meaningless, although both basis sets are of double zeta quality.

For comparing energies at different geometries, nuclear-fixed basis set introduces an error. This is because the quality of basis set is not same at all geometries, since electron density around one nucleus may be described by functions centered at another nucleus. This is especially troublesome when calculating small effects, such as energies of Vander Waals complexes and hydrogen-bonds.

It is also observed that CP (Car and Parrinello) corrections for methods including electron correlation are larger and more sensitive to the size of the basis set than at the HF level. The HF wave function converges much faster concerning the size of the basis set than correlated wave functions.

Chemical Hamiltonian Approach (CHA), methods are not commonly used yet. For intramolecular cases, it is difficult to define a unique procedure for estimating the BSSE (basis set superposition error). Performance of functional is not same for two sets of results. A minor part of this difference is due to the difference in basis sets, and remaining difference is due to the difference in data sets.

2.6 Magnetic Exchange

The net spin state of metal ion that interacts with the nearby spin and gives a particular type of electronic exchange (ferromagnetic or antiferromagnetic) interaction is mentioned as Heisenberg magnetic exchange (*J*). Hoffmann and Kahn's model's[61] are the active electron approximation, in which only unpaired electrons are considered, core electrons are neglected. In these models, spin-orbit interactions are considered, the minimal basis set under *semi-empirical* methods to evaluate the integrals. As a result, these models give a poor estimate of *J* value compared to experiments, though these models are widely used to interpret the magnetic properties. Magnetic exchange interactions are calculated in two different spin state centers in metal or in between the metal center and radical. These are calculated by employing the following spin Hamiltonian,

$$\hat{H} = -J\, \mathbf{S_1}.\mathbf{S_2} \qquad (2.18)$$

Where, S_1 and S_2 denote the total spin of the individual center, and *J* is the magnetic exchange coupling constant.

The magnetic exchange is calculated by energy of the high spin (intermediate spin and low spin) state and their corresponding broken symmetry.[62] Ruiz *et al.* provide a very good methodology for the estimation of *J* values.[63-64] Positive and negative *J* value, indicates ferromagnetic and antiferromagnetic interaction.

2.7 Natural Bond Orbital (NBO) Analysis

The natural bond orbital analysis uses the many bonds wave functions in terms of localized electron pairs.[65] NBO is the name of a whole set of analysis techniques. It determines the natural atomic orbitals (NAO), natural bond orbitals (NBO), natural localized molecular orbitals (NLMO) and uses these to analyze natural population analysis (NPA), NBO energetic analysis of wave function properties, natural resonance theory (NRO) and natural chemical shielding (NCS) analysis.

One of these is the natural population analysis (NPA) for obtaining occupancies and charges. NBO uses the natural orbitals instead of molecular orbitals directly. Natural orbital is the eigenfunctions of the first-order reduced density matrix. The eigenfunctions of the second-order density matrix are called Natural Germinals. For single-determinant RHF wave function, in which natural orbitals have the occupation number exactly either 0 or 2. While for the multi-determinant wave function and UHF, the occupation number is fractional in between 0 and 2. The natural orbital provides the fastest convergence. Natural atomic orbital (NAO) and Natural Bond Orbital (NBO) analysis was developed by Weinhold and coworkers and these use the one-electron density matrix for defining the atomic orbitals in the molecular environment and derive the molecular bond by electron density between them. These are localized for achieving well-defined division of the electrons, the orbitals should be orthogonalized.

NBO analysis is based on a method of transformation of a given wave function into localized form, corresponding to one-center (lone pair) and two-center (bond) elements of Lewis structure.

The order of transformations of the input atomic orbital basis set.[66-68]

$$AOs \rightarrow NAOs \rightarrow NHOs \rightarrow NBOs \rightarrow NLMOs$$

Based on the magnitude of occupation number the natural atomic orbital may be divided into a "natural minimal basis" (having occupation number significantly different from zero) and "Rydberg" (having occupation number close to zero) orbitals. Analysis of basis function allows classifying the transformed orbitals as bonding, antibonding, core, and Rydberg orbitals. There is also a procedure for the resonant system which predicts the π bonding in such systems.

Second-order perturbative estimates the donor-acceptor (bond-antibond) interaction on NBO basis. For this analysis, all the possible interactions between "filled" Lewis-type NBOs (donor, L) and "unfilled" (acceptor, NL) non-Lewis type NBOs are examined. These interactions lead to loss of occupancy from idealized Lewis structure localized NBO to empty non-Lewis orbital; this is known as "delocalization" correction to zeroth-order natural Lewis structure. Donor-acceptor stabilization E(2) from donor NBO (i) to acceptor NBO (j) is given by

$$E(2) = \Delta E_{ij(2)} = \frac{q_i F(i,j)}{(E_j - E_i)} \tag{2.19}$$

Where, q_i is the donor orbital occupancy (2 for closed-shell, 1 for open-shell) E_i and E_j are diagonal elements (orbital energies), and F(i,j) is the off-diagonal NBO Fock matrix element. This is a popular technique that is available in many software packages and is easy to understand. It is a convenient method to classify the type of orbital.

2.8 Solvation

In quantum chemistry, basis calculations are performed in gas-phase, assuming that the interaction between the model complex and surrounding medium is negligible. However, most natural and laboratory reactions do not occur in a vacuum, the reaction occurs in the solution that means interaction between solute and solvent particles exist. The solute

properties such as structure, stability, spectra, and reactivity depend on the solvent, particularly a polar one. Computational chemistry also evaluates the environment, of solvent. Methods for evaluating solvent effects are mainly two types: One describes the individual solvent molecules and the other treats the solvent as a continuous medium.[69-71] Combinations of these two are also possible, for example considering explicit first shell and remaining as a continuum model. Solvent effects are mainly of two types one is long-range (non-specific) and the other is short-range (specific) effect. Solvent polarization and orientation of dipole are long-range effects whereas hydrogen bonds, Vander Waals interaction, solvent-solute dynamics, charge transfer effects and hydrophobic effects are short-range solvation effects. Methods, in which solvent molecules are explicitly described, required a sampling of phase space. These methods are computationally expensive, thus there is strong interest to develop methods, in which solvent is modeled in gentle fashion.

Langevin dynamics method takes into account the average solute-solvent dynamics. By considering the solvent as a homogenous medium having a dielectric constant, the solvation non-specific effects can be modeled.

Continuum Solvation Models

Continuum models[72] consider the solvent as a uniform polarizable medium with a dielectric constant(ε). The dielectric constant is the characteristic property of a solvent. For a given medium value of the dielectric constant is fixed. While in dynamic phenomena it is taken as dependent on frequency.[73] Solvent having the same dielectric constant value are treated equally. For example acetone ($\varepsilon = 20.7$) and propan-1-ol ($\varepsilon = 20.1$), or benzene ($\varepsilon = 2.28$) and carbon tetrachloride ($\varepsilon = 2.24$) are nearly equal. But, in reality, the hydrogen bonding capability of propan-1-ol is different from acetone while the dynamics of spherical carbon tetrachloride is different from that of planar benzene.

The self-consistent reaction field (SCRF)[74-76] is a solvation model which is based on Onsager's reaction field theory.[77] In this model, solvent containing the solute molecule turns a cavity into a polarized form. The main drawback of this model is that the solvent effect will not be observed for the system having zero dipole moment.

The polarized continuum method (PCM) is the most popular self-consistent reaction field (SCRF) method, developed by Tomasi and coworkers. In the PCM method, a spherical cavity around each atom is used, and numerical integration over the solute charge density is used. Several variations use the nonspherical cavity. This method is widely used because of its good results in a cost-effective manner and applies to the arbitrary solute. However, it is sensitive towards the basis set used.

The conductor-like screening model (COSMO) is a continuum method based on solvent-accessible surface and it is fast. It can be used with a variety of semi-empirical, *ab initio,* and DFT methods. Cavity construction differs in different COSMO implementations and it is constructed as an assembly of atom-centered spheres with radii having 20% greater than the Vander Waal interaction. In real calculations, the cavity surface is approximated by segments, e.g., hexagons, pentagons, or triangles. By determining the charge distribution of the molecule, and the solvent charge, the interaction energy between solute and solvent can be calculated.

2.9 Reaction Mechanism

Transformation of one species to another takes place in elementary steps and this is called reaction mechanism.[78] Reaction mechanism is the description; step to step that occurs during the reaction at every stage of the reaction. It also describes the reactive intermediates, and the transition states. Reactive intermediate is a stable geometry and exists at the minimum of the energy occurring during the reaction and has a lifetime in order of 10^{-13} and 10^{-14} sec and

these are often radicals or ions.[79] Transition states are the unstable molecular entities involved during the reaction and these have an unstable number of bonds and unstable geometry. These correspond to the maxima on the reaction coordinates.

The rate of a reaction depends upon the concentration of the reactant. The bimolecular reaction between *a* moles of A and *b* moles of B is given below;

$$aA \quad + \quad bB \quad \rightarrow \quad products \tag{2.20}$$

The rate expression for the above reaction can be given by;

$$r = k[A]^a[B]^b \tag{2.21}$$

Where, k is rate constant, it is independent of the concentration of reactant, it depends only on the reaction temperature, and by the Arrhenius equation rate constant k is given by

$$k = Ae^{-E_a/RT} \tag{2.22}$$

Where, E_a is the activation energy and A is called the pre-exponential factor.

As the higher value of k, indicates faster will be the reaction, lower the value of k slower be reaction and for the intermediate value of k moderate will be the reaction rate. It is necessary to know the factors affecting reaction rate for understanding the reaction mechanism.

2.9.1 Transition state theory

Eyring, Polanyi, and Evans in 1935 developed the Transition state theory (TST). It is also known as absolute reaction rate theory (ARRT) and activated complex theory (ACT) and this is used to calculate the reaction rate of a chemical reaction and describe how a reaction can occurs.

TST is based on many mathematical assumptions. It assumes that Maxwell-Boltzmann statistics predict that how many molecular collisions have energy equal to or greater than the activation energy i.e. the molecules at transition structure are in equilibrium with the reactant,

it is known as quasi-equilibrium. It also assumes that at the transition state molecules react irreversibly. Consider a reaction

$$A + B \underset{}{\overset{K^{\#}}{\rightleftharpoons}} R \longleftrightarrow TS \xrightarrow{k'} C + D \rightleftharpoons P \qquad (2.23)$$
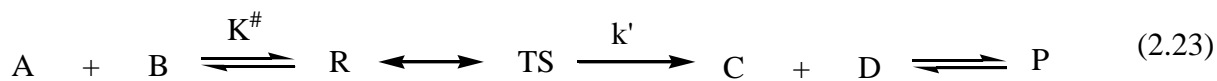
$$K^{\#} = \frac{[TS]}{[R]} \qquad (2.24)$$

$$[TS] = K^{\#}[R] \qquad (2.25)$$

$K^{\#}$ is the equilibrium constant between the reactant and the transition state.
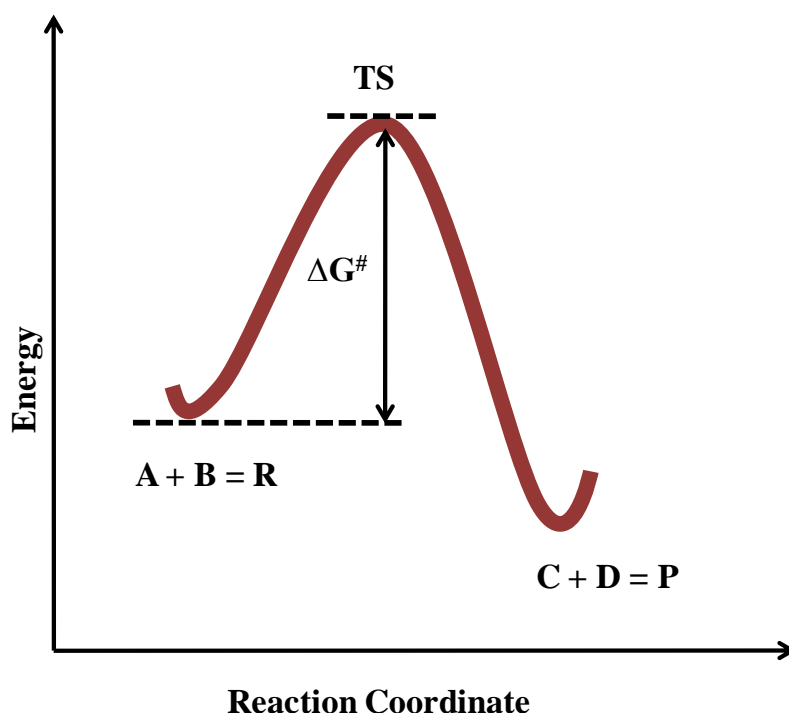

Figure 2.5. The chart showing the PES of an elementary single-step bimoleculer reaction.

From the classical mechanics, the energy of vibration is given by RT/N_A whereas from quantum mechanics it is given by $h\upsilon$. Thus,

$$h\upsilon = \frac{RT}{N_A} \qquad (2.26)$$

$$\upsilon = k_B T/h \qquad \text{Where, } R = k_B N_A \qquad (2.27)$$

The vibrational frequency υ is the rate at which the activated complex molecules move across the energy barrier. Thus, the rate constant k_2 can be identified by υ.

The reaction rate is given by,

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$$-\frac{d[A]}{dt} = kk'[TS] \tag{2.28}$$

$$-\frac{d[A]}{dt} = k\left(\frac{K_B T}{h}\right)[TS] \tag{2.29}$$

Where k, is the transmission coefficient, which is a measure of the probability that a molecule, passes over the barrier, will keep on going ahead and do not return. It can be omitted from rate expression as its value is taken as unity.

$$-\frac{d[A]}{dt} = \left(\frac{K_B T}{h}\right)K^{\#}[R] \tag{2.30}$$

Rate constant k' can be expressed as

$$k' = \left(\frac{K_B T}{h}\right)K^{\#} \tag{2.31}$$

The equilibrium constant $K^{\#}$ can be expressed in terms of $(G°)^{\#}$, called the standard Gibbs free energy of activation. Since, for the activated complex, we can write

$$(G°)^{\#} = -RT \ln K^{\#} \tag{2.32}$$

$$K^{\#} = e^{-(G°)^{\#}/RT} \tag{2.33}$$

Rate constant can be given by

$$k_{rate} = \left(\frac{K_B T}{h}\right)e^{-(G°)^{\#}/RT} \tag{2.34}$$

Where,

Boltzmann constant $(K_B) = 1.38 \times 10^{-23}$ J/K

Planck`s constant (h) $= 6.63 \times 10^{-34}$ Js

Gas constant (R) $= 8.314$ J K^{-1} mol^{-1}

Temperature (T) = in Kelvin

$(G°)^{\#}$ = difference in Gibbs free energy between reactant and the transition state theory is characterized by one imaginary frequency

$\Delta G^{\#}$ = calculated at the saddle point of Born-Oppenheimer free energy surface

2.10 Gaussian

The most widely used program in computational chemistry is Gaussian. It was released by John Pople in 1970. This name is given because Pople's use the Gaussian orbitals to speed up the calculations of molecular structure. It is a suite of programs with *ab initio*, density functional theory, semi-empirical, molecular mechanics, and various hybrid methods for predicting many properties of the atom, molecule, and reactive systems including molecular energies, structures, transition states, vibrational frequencies, IR, Raman spectra, thermochemical properties, reaction pathways, molecular orbitals, atomic charges, multipole moments, NMR shielding, magnetic susceptibilities, vibrational circular dichroism intensities, electron affinities, ionization potentials, polarizabilities and hyperpolarizabilities, electrostatic potentials and electron densities.

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