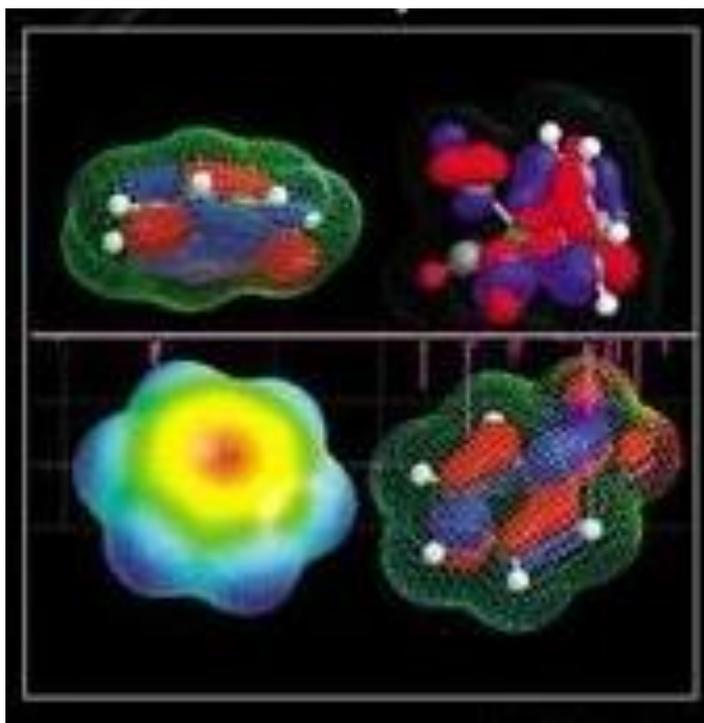


## CHAPTER - 3



## QUANTUM CHEMICAL CALCULATIONS AND NORMAL COORDINATE ANALYSIS

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## CHAPTER - 3

### 3.1 INTRODUCTION

Quantum chemistry and computer modeling plays a major role in vibrational spectroscopic research. Vibrational spectroscopy is perhaps the most versatile and yet a relatively simple and cheap instrumental method of structural analysis that is applied in virtual all branches of chemistry, in particular to the growth of polymer chemistry, molecular confirmation, reaction kinetic, design of new drugs and material.

The philosophy of computational methods of vibrational spectroscopy (Willson *et al.*, 1995; Cyvin., 1968) changed significantly when quantum mechanical programmers for optimization of the geometry of a molecule and for analytical determination of its force field appeared. Harmonic force fields derived from quantum mechanics are widely used at present for the calculation of frequencies, intensities of spectral bands with a minimum degree of arbitrariness (although the degree depends on the level of the quantum-mechanical treatment) and the modes of normal vibrations.

Though, in numerous existing quantum mechanical measurements, vibrational spectra at various levels of approximation, calculated frequencies are higher than their experimental equivalents. This outcome is due to the more or less systematic overestimation of the force constants in the Hartree-Fock (HF) method (Hehre, 1986). This overestimation of the force constants depends on the basis set employed (Bock *et al.*, 1990) and to the not-so-regular discrepancies in applications of the Moller-Plesset (MP) theory (Moller, 1934). These calculations required empirical corrections. To enhance the agreement with experiment, quantum-mechanical force fields are good in one way or another, e.g. using empirical corrections called scale factors, which are found to be estimated from the experimental vibrational spectra of small molecules with reliable frequency assignments.

Second-order Moller-Plesset perturbation theory (MP2) cannot completely take the correlation energy of a system into account (the more so when restricted basis sets are used). Thus, this theory does not obviate the requirement of scaling force constants. Moreover, some molecules having hetero atoms especially halogens (De Mare and

Panchenko., 1994), this approximation results in irregular deviations of calculated frequencies from experiment.

In recent days, sophisticated electron correlation calculations are increasingly available and deliver force fields of increased accuracy for small polyatomic molecules. The scaled quantum mechanical (SQM) and force fields (Pulay., 1983) are of analogous accuracy with the best purely theoretical results. In addition, the scaling procedure fits the force field to experimental (anharmonic) frequencies. Therefore, the reproduction of observed spectra will be much better with an SQM force field than with the best harmonic field.

Molecular mechanics deals with the alterations in the electronic energy of the molecule due to bond stretching ( $V_b$ ), bond angle bending ( $V_\theta$ ), out-of-plane bending ( $V_{o\theta}$ ), internal rotation (torsion) about bonds ( $V_\phi$ ), interactions between several kinds of motions ( $V_{int}$ ), Van der Waals attraction and repulsion between non-bonded atoms ( $V_{vdw}$ ) and electrostatic interactions between atoms ( $V_{es}$ ). The total sum of these contributions provides the potential energy in the molecular mechanics frame work  $V$  for the motion of the atoms in the molecules. It is then termed as the steric energy or strain energy for the motion of atoms present in the molecules. The mathematical form of this energy function (also referred as potential energy surface) is given -

$$V(X^N) = \sum_{i=1}^k V_i \quad (3.1)$$

Where  $V$  depicts the potential energy of the molecular system, which is a function of the Cartesian coordinates of all atoms denoted as  $X^N$ . The parameters of the energy functions must be known in advance for all type of energy terms consisting of the molecular systems.

The equation (3.1) can be written as

$$V = V_b + V_\theta + V_{o\theta} + V_\phi + V_{int} + V_{vdw} + V_{es} \quad (3.2)$$

### 3.2 GEOMETRY OPTIMIZATION

A known molecular formula can symbolize a number of molecular isomers. Every isomer is a local minimum on the energy surface (known as potential energy surface) bent from sum energy (electronic energy + repulsion energy present in between the nuclei) as a purpose of the co-ordinates of all nuclei. A stationary point is a geometry such that the derivative of the energy with deference to all displacements of the nuclei is ordinal. A local minimum (energy) is a stationary point where all such displacements lead to an increase in energy. The local minimum that is lowest is termed as the global minimum and corresponds to the most constant isomer. If there is one particular coordinate alters, results in a decline of the total amount of energy in both directions, the stationary point is a transition structure and the coordinates are the reaction coordinate. This process of determining stationary points is known as geometry optimization. This optimized structure serves as an excellent starting point for molecular dynamics.

The principle behind molecular structure by geometry optimization became customized when resourceful methods for measuring the first derivatives of the energy owing to all atomic coordinates became available. Determination of the associated second derivatives permits the prediction of vibrational frequencies if harmonic motion is assumed. In some ways more importantly it allows the characterization of the stationary points. The frequencies are related to the eigen values of the matrix of second derivatives (The Hessian Matrix). If there is a positive eigen values, then the frequencies are all real and the stationary point is a local minimum. If one eigen value is negative (an imaginary frequency), the stationary point is a transition structure. If more than one eigen values is negative, the stationary point is a more complex one, and usually of little interest. It is required to shift the search away from it, if we are looking for local minima and transition structures.

### 3.3 COMPUTATIONAL TECHNIQUES

Computational techniques consist of three areas: Ab initio methods, semi-empirical methods, and molecular mechanics. Molecular mechanics utilizes classical physics to solve large systems of molecules and is considered the least accurate due to the fact that no electron behavior is factored in semi-empirical methods are more accurate because of utilization of quantum physics to account for some of the electron behaviour, but its scope is still limited since it relies on extensive approximations and empirical parameters. Ab initio methods are based purely on quantum physics and use no approximation from classical physics to describe the electronic structure of the molecule very accurately. The drawback of using ab initio methods is that the computations are extremely taxing and it is limited to much smaller systems such as individual molecules. However, ab initio methods give a lot of information on the electronic structure without having to actually synthesize the molecule experimentally. The fundamental idea behind ab initio calculations is to solve Schrodinger's equation with a set of mathematical functions called a "basis set".

#### 3.3.1 Ab initio Methods

The term 'Ab initio' means from first principles. It does not mean that we are solving Schrodinger equation exactly. It means selecting a method that in principle can lead to a reasonable approximation to the solution of the Schrodinger equation and then selecting a basis set will implement the method in a reasonable way and we depict that the results are fine and sufficient for the purpose in hand.

A basic method and preliminary set that is quite sufficient for one application may be totally inadequate for another application. We also have to receive into account the cost of doing calculations and the total quantity of computer time required. The most famous ab initio methods are Moller-Plesset (MP) perturbation, Hartree-Fock (HF), Couple-Cluster (CC) and Density Functional Theory (DFT). There are several differences in opinion about if DFT has to be considered solely ab initio or semi-empirical method.

Hartree-Fock method is one of the widely used approximation method. It is based on the ordinary estimation that every electron moves in the potential shaped by the nucleus plus the standard potential of all the other electrons. This assumption results in the independent particle model, which functionally reduces many electrons to the problem of solving a number of coupled single-electron equation. The single-electron equations are solved in an iterative manner until a chosen level of self-consistent accuracy is attained. The HF approximation is a fast and reliable method for a diverse range of atomic system, but it is just a preliminary estimation. There are several calculation schemes urbanized to promote improved results.

Certain limitations of HF calculations are that they do not consist of electron correlation. This means that HF taken into accounts the average effect of electron repulsion, but not the explicit of electro-electro interaction. We call this effect as “correlation”. The difference in energy between the exact result and the HF limit energy is called the “correlation energy”. The energies calculated are usually in units called Hartree ( $1H=27.2114$  eV). The energies are always greater than the energy and approach a limiting value called the Hartree-Fock limits.

The “Hartree-Fock” has the best HF wave function and is rich with such a large and flexible basis set. Ab initio orbital molecular methods are helpful to envisage harmonic force constants and frequencies of normal modes. The Ab initio methods tend to optimize the molecular geometry and then assess the second derivative at the equilibrium positions generally using analytical derivatives. Such methods supply reliable values for harmonic vibrational frequencies for fairly great sized molecules. Additionally, such calculations can be used to identify barriers to internal rotation as well as relative stabilities of various conformers. The information received from structural parameters, force constants, conformational stabilities, vibrational frequencies as well as infrared and Raman band intensities gives momentous contributions to the field of vibrational spectroscopy.

Harmonic force constants in Cartesian coordinates can be derived directly from ab initio calculations. These force constants can be converted to force constants in internal or symmetry coordinates. Ab initio calculations followed by normal coordinate

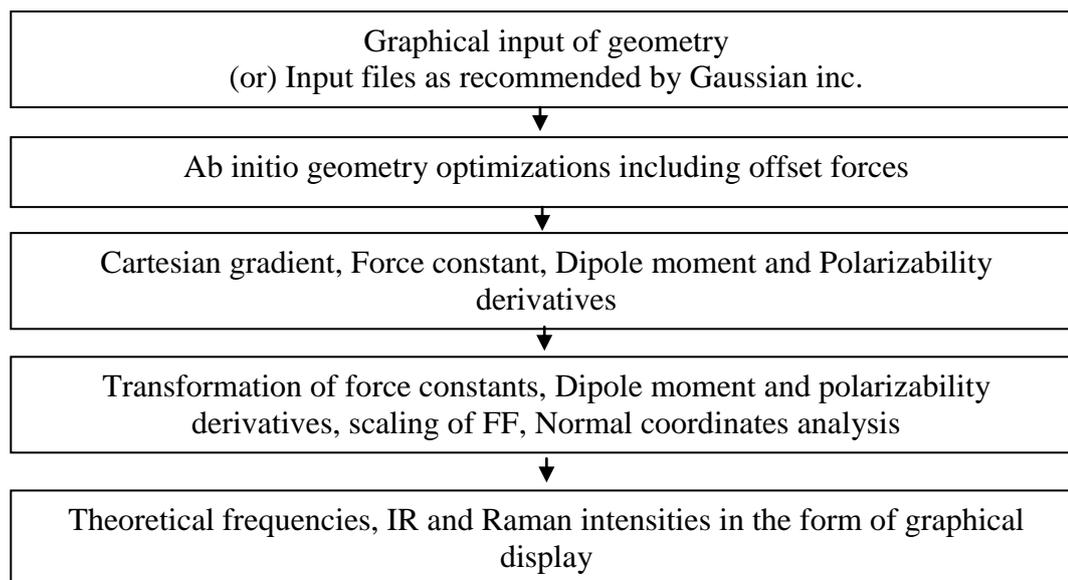
analysis are very useful in making reliable vibrational assignments. Band intensities from Ab initio studies are another significant output. Such type of band intensity data can also be very useful in making vibrational assignments. Two principally different quantum mechanical methods addressing the vibrational problems are namely HF method and density functional theory (DFT). Density functional theory calculation has emerged in the past few years as successful alternative to traditional HF method. The DFT methods, particularly hybrid functional methods (Shin *et al.*, 1998; Par and Yang., 1989) have evolved as a powerful quantum chemical tool for the determination of the electronic structure of the molecules. In the scaffold of DFT approach, various exchange and correlation functional are routinely used. Among these, the Becke-3-Lee-Yang-Parr (B3LYP) combination (Becke., 1993; Lee., 1988) is the most used since it proved its capacity in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and several standard basis sets, provide an outstanding compromise between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The vibrational frequencies measured by applying DFT methods are functionally overestimated than experimental values by 5-2% on an average. This over estimation is owing to the neglect of electron correlation, anharmonicities and incomplete basis sets.

This over estimation can be narrowed down by applying empirical corrections called scaling, where the empirical scaling factors are ranging from 1.0 to 0.8. The scaling factors depend both on method and basis sets and they incompletely compensate for the systemic errors in the calculation of frequencies. Global scaling or uniform scaling, multiple scaling or selective scaling is some scaling methods advocated to reduce the overestimation of the frequency differences. Ab initio calculation could be performed using Gaussian 09W Software package (Frisch *et al.*, 2008)

If the quantum mechanical force field is not corrected, especially in the case of large deviations from the experimental results, this emission can complicate the theoretical analysis of the vibrational spectrum of a molecule leading to the mistakes in the assignment of the experimental frequencies. Therefore, evaluating the empirical corrections to quantum mechanical force fields is significant. It is found that, among all the methods for empirically correcting quantum mechanical force fields, the one with

the better physical basis is the contemporary version of the Pulay method (Panchenko., 1997).

A simple flow chart (Figure 3.1) which explains the entire scheme of calculation by quantum chemical methods is given below-



**Figure 3.1** Flow chart of programme used in the quantum chemical calculations

### 3.3.2 Moller-Plesset Perturbation Methods

Moller-Plesset perturbation theory (MP) is one of the several quantum chemistry post-Hartree-Fock (post-HF) Ab initio methods in the field of computational chemistry. Any method which goes beyond HF in attempting to treat central field approximation properly is known as an electron correlation method or a post-HF method. It improves HF method by adding electron correlation effects through Rayleigh-Schrödinger perturbation theory (RS-PT), generally to second (MP2), third (MP3) or fourth (MP4) order. Its main focus was published as early as 1934 by Moller and Plesset (Moller., 1934). Correlation can be added as a perturbation from the HF wave function. This is called Moller-plesset perturbation theory (MPPT). The HF wave function onto a perturbation theory formulation in mapping, becomes a first-order perturbation. Thus, a minimum amount of correlation is added by using the second-order MP2 method.

The MPPT assumes that the effects of electron correlation are minor, and can be described by small corrections (perturbations) to the HF solution.

An alternative to multi-electron wave functions is to choose an approximation for the correlation energy. In this theory, an additional term is added to the total energy and is treated as a perturbation. The perturbed wave function and perturbed energy are expressed as a power series to the  $n^{\text{th}}$  order (MPn) such as MP2, MP4 etc, although it is not always convergent with increasing the power n.

### 3.3.3 Semi-Empirical Methods

Semi-empirical calculations are, like Ab initio, based on the Schrodinger equation. Here more approximations are made in solving it. The most intricate integrals that must be calculated in the Ab initio method are not really determined in SE calculations instead the program draws with a kind of library of integral that was complicated by finding the best fit of some calculated entity like geometry or energy to the experimental values. This plugging of experimental values into mathematical procedures to get the best calculated values is called parameterization. SE calculations are slower than molecular mechanics method but much faster than ab initio calculations. Some SE methods are self-consistent procedure (SCF) and dewar group. The SCF methods are simple huckle method (SHM), extended huckle method (EHM), the Parisar-Parr-pole (PPP) method and the complete neglect of differential overlap (CNDO) method and Dewar group methods are neglect of diatomic differential overlap (NDDO) method, modified NDDO (MNDO) method, Austin method 1 (AM1), parametric method 3 (PM3) and semi Abinitio method 1 (SAM1).

### 3.3.4 Density Functional Theory

Density functional theory (DFT) is a quantum mechanical modeling method worn in physics and chemistry to investigate the electronic structure of many body systems, in particular atoms, molecules and the condensed phases. DFT is among the most accepted and versatile methods available in condensed matter of physics and computation chemistry.

Conventional methods in electronic structure theory, in particular HF theory and its descendants, are based on the complicated many electron wave function. The main objective of density functional theory is to replace the many body electronic wave functions with the electron as the basic quantity whereas, many body wave functions is dependent on  $3N$  variables, three spatial variables for each of the  $N$  electrons, the density is only a function of three variables and is a simpler quantity to deal with both theoretically and practically.

Although, density functional theory has its conceptual roots in the Thomas-Fermi model, DFT was put on a firm theoretical footing by Hohenberg and Kohn theorem. The first theorem demonstrates the subsistence of a one to one mapping between the ground state electron density and the ground state wave function of a many particle system. The second theorem proves that the ground state density reduces the total electronic energy of the system. The most general implementation of density functional theory is through the Kohn-Sham method. Within the stipulated work of Kohn-Sham DFT, the intractable issues of the body interacting with electrons in a stable external potential is minimized to a tractable issues of non-interacting electrons moving in an effectual potential. It includes the external potential and the effects of the coulomb interactions between the electrons, e.g. the exchange and correlation interactions.

### 3.3.5 Derivation and Formalism of DFT

In Born-Oppenheimer approximation, the electronic structure of body measurements, with the nuclei of the treated molecules or clusters are seen unchanging generating a static external potential  $V$  in which the electrons are keep moving. A stationary electronic state is then described by wave functions  $\Psi(\vec{r}_1, \dots, \vec{r}_N)$  fulfilling several electrons by Schrodinger equation.

$$H\Psi = [T + V + U]\Psi = \left[ \sum_i^N -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j) \right] \Psi = E\Psi \quad (3.3)$$

Where  $H$  is the electronic molecular Hamiltonian,  $N$  is the number of electrons and  $U$  is the electron-electron interaction. The operators  $T$  and  $U$  are known as universal

operators as they are similar for any system, while  $V$  is system dependent or non-universal. As one can see, the actual variation between a single particle problem and the much more complicated particle problem just arises from the interaction term  $U$ . There are several sophisticated methods for solving the many-body Schrodinger equation based on the expansion of the wave function in Slater determinants. While the simplest one is the HF method, are more sophisticated approaches that are generally categorized as post-HF methods. However, the problem with these methods is the huge computational effort, which makes it practically impossible to apply them efficiently to larger, more complicated systems.

DFT provides an engaging substitute, being much more stretchy as it leaves a path to methodically map many-body problem, with  $U$ , onto a single-body problem without  $U$ . The variable in DFT is the particle density  $n(\vec{r})$  which is represented by,

$$n(\vec{r}) = N \int d^3r_2 \int d^3r_3 \dots \int d^3r_N \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \quad (3.4)$$

Hohenberg and Kohn proved in 1964 (Hohenberg and Kohn., 1964) that the relation expressed above can be reversed i.e. to yield ground state density  $n_0(\vec{r})$  is in principle to measure the corresponding ground state wave function  $\Psi_0(\vec{r}_1, \dots, \vec{r}_N)$ . In certain other words,  $\Psi_0$  is a unique functional of  $n_0$ , i.e.

$$\Psi_0 = \Psi_0[n_0] \quad (3.5)$$

and subsequently all other ground state observable  $O$  are also functional of  $n_0$

$$\langle O \rangle [n_0] = \langle \Psi_0[n_0] | O | \Psi_0[n_0] \rangle. \quad (3.6)$$

From this, the ground state energy is a functional of  $n_0$

$$E_0 = E[n_0] = \langle \Psi_0[n_0] | T + V + U | \Psi_0[n_0] \rangle \quad (3.7)$$

Where, the input of the external potential  $\langle \Psi_0[n_0] | V | \Psi_0[n_0] \rangle$  can be represented explicitly in terms of the density.

$$V[n] = \int V(\vec{r}) n(\vec{r}) d^3r. \quad (3.8)$$

The functions  $T[n]$  and  $U[n]$  are known as universal functions while  $V[n]$  is obviously non-universal, as it depends on the system under study. Having specified a system, i.e.  $V$  is known, which has to reduce the functional is,

$$E[n] = T[n] + U[n] + \int V(\vec{r}) n(\vec{r}) d^3r. \quad (3.9)$$

With respect to  $n(\vec{r})$ , assuming one has got reliable expressions for  $T[n]$  and  $U[n]$ . A conquering reduction of the energy functional will give the ground state density  $n_0$ , and thus all other ground state is observable.

The variational problem of minimizing the energy functional  $E[n]$  can be solved by applying the Lagrangian method of undetermined multipliers, which was done by Kohn and Sham in 1965 (Kohn and Sham., 1965). The function in the equation (3.9) can be printed as a fictitious density functional of a non-interacting system.

$$E_s[n] = \langle \Psi_s[n] | T_s + V_s | \Psi_s[n] \rangle, \quad (3.10)$$

Where  $T_s$  denotes the non-interacting kinetic energy and  $V_s$  is an external effective potential in which the particles are moving. Obviously,  $n_s(\vec{r}) \equiv n(\vec{r})$  if  $V_s$  chosen to

$$V_s = V + U + (T - T_s) \quad (3.10a)$$

Thus, one can resolve the so-called Kohn-Sham equations of this auxiliary by non-interacting system

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}), \quad (3.11)$$

Which produces the orbitals  $\phi_i$  that duplicate the density  $n(\vec{r})$  of the original many body system.

$$n(\vec{r}) \equiv n_s(\vec{r}) = \sum_i^N \left| \phi_i(\vec{r}) \right|^2 \quad (3.11a)$$

The effective single-particle potential  $V_s$  can be represented in more detail as

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + V_{xc} [n_s(\vec{r})] \quad (3.12)$$

Where, the second term of equation (3.12) denotes, Hartree term describing the electron Coulomb repulsion, while the last term  $V_{xc}$  is called the exchange correlation potential. Here,  $V_{xc}$  includes all the many-particle interactions. The Hartree term and  $V_{xc}$  depend on  $n(\vec{r})$ , depends on the  $\phi_i$ , which in turn depend on  $V_s$ , and the problem of solving the Kohn-Sham equation has to be done in an iterative way. Usually one starts with an initial guess for  $n(\vec{r})$ , then calculates the corresponding  $V_s$  and solves the Kohn-Sham equations for  $\phi_i$ . From these values, a novel density value can be calculated and the entire phenomena are repeated until a convergence is reached.

### 3.3.6 Applications of DFT

Kohn-Sham theory can be applied in different distinct ways depending on what is being explored. In molecular calculations, a huge variety of exchange-correlation functionals have been developed for chemical applications. A popular functional widely used is B3LYP (Becke., 1993; Lee *et al.*, 1988; Stephens *et al.*, 1993) which is a hybrid method in which the DFT exchange functional, is combined with the exchange functional from HF theory. These hybrids are functional which carries modifiable parameters, which are normally fitted to a train a set of molecules.

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**(i) Exchange Functionals**

Names for the various pure DFT models are given by combining the names for the exchange and correlation functional as follows

Becke 88 (B)–Becke's (1988) functional, which includes the Slater exchange along with corrections involving the gradient of the density.

Barone's Modified PW91(MPW)–The Perdew-Wang (1991) exchange functional as modified by Adamo and Barone.

Gill96(G96)–The 1996 exchange functional of Gill.

The combination forms were used when one of these exchange functional is used in combination with a correlation functional see below.

VWN –Vosko, Wilkand Nusair 1980 correlation functional (III) fitting the RPA solution to the uniform electron gas, often referred to as local spin density (LSD) correlation.

VWN V (VWN5)–Functional V from the VWN80 paper which fits the Ceperley-Alder solution to the uniform electron gas which is the function recommended in the paper.

LYP(LYP)–The correlation functional of Lee, Yang, and Parr, which includes both local and non-local terms.

Perdew Local (PL)–The local (non-gradient corrected) functional of Perdew (1981).

Perdew 86P(P86) –The gradient corrections of Perdew, along with his local correlation functional (1981)

Perdew/Wang 91(PW91) –Perdew and Wang's (1991) gradient-corrected correlation functional.

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Becke 96(B96) –Becke's (1996) gradient-corrected correlation functional (part of his one parameter hybrid functional).

All of the efficient words for these correlation functionals must be linked with the keyword for the preferred exchange functional. For example, BLYP desires the Becke exchange functional and the LYP correlation functional. SVWN needs the Slater exchange and the VWN correlation functional, and is termed in the literature by its synonym local spin density approximation (LSDA).

### **(ii) Hybrid Functionals**

Three hybrid functionals which include a mixture of Hartree-Fock exchange with DFT exchange-correlation are available via keywords as follows

Becke's Three Parameter Hybrid Functional using the LYP Correlation Functional(B3LYP) - BRUKER IFS 66V, FT-IR with FRA 106FT-Raman spectrophotometer. This is Becke's 3 parameter functional (Becke., 1993), where the non-local correlation is provided by the LYP expression. Rather than VWN functional III and LYP, he used LDA densities and the Perdew/Wang (1991) correlation functional. Since LYP includes both local and non-local terms. In further words, VWN is used to supply the surplus local correlation required, since LYP consists of a local term significantly equivalent to VWN.

Becke's Three Parameter Hybrid Functional with Perdew 86 (B3P86) –This is Becke's 3 parameter functional as above, with the non-local correlation provided by the Perdew 86 expression.

Becke's Three Parameter Hybrid Method Functional with Perdew/Wang 91(B3PW91) –This is Becke's 3 parameter functional, with the non-local correlation provided by the Perdew 91 expression.

Becke's One Parameter Hybrid Functional with Becke's 1996 Correlation Functional(B1B96) –This is Becke's one-parameter hybrid functional as defined in the original paper (Becke., 1996).

Becke's One Parameter Hybrid Functional with LYP Correlation (B1LYP)–Becke's one parameter hybrid functional using the LYP correlation functional (as described for B3LYP above) as implemented by Adamo and Barone (Becke., 1996; Adamo and Barone., 1997).

One Parameter Hybrid Functional with Modified Perdew-Wang Exchange and Correlation (MPW1PW91) –Barone and Adamo's Becke-style one parameter functional using modified Perdew-Wang exchange and Perdew-Wang 91 correlation (Adamo and Barone., 1997).

Barone and Adamo's - One Parameter Hybrid Functional with Gill 96 Exchange and LYP Correlation (G961LYP). Becke- style is one parameter functional using Gill 96 exchange and LYP correlation (Adamo and Barone., 1998).

### **3.4 BASIS SET**

In modern quantum, chemical calculations are classically performed within a finite set of basis functions. Gaussian 09W and other ab initio electronic structure programmes use Gaussian type atomic functions as basis functions. A basis set is the mathematical portrayal of the orbitals within a system (which in turn merge to approximate the total electronic wave functions) used to perform theoretical calculation. The wave functions under contemplation are all depicted as vectors, the components of which correspond to coefficients in a straight linear combination of the basis functions in the basis set used. The operators are then depicted as matrices, in this finite basis.

When molecular calculations are performed, it is frequent to utilize the basis composed of a finite number of atomic orbitals, centered at each atomic nucleus within the molecule. Initially, atomic orbitals were usually Slater orbital, which corresponds to a set of functions, which perished exponentially with distance from the nuclei. These Slater-type orbitals (STO) could be approximated as linear combinations of Gaussian orbitals. It is much more easier to compute overlap and other integrals with Gaussian basis functions and this led to excessive computational savings of the basis sets composed of Gaussian-type orbitals (GTOs), the smallest are called minimal basis sets

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and they classically composed of the minimum number of basis functions needed to characterize all of the electrons on each atom.

The most general addition to minimal basis sets in the addition of polarization functions, denoted by an asterisk, \*. Two asterisks, \*\*, that indicate the polarization functions which are also added to light atoms (Hydrogen and Helium). When polarization is added to this basis set, a p-function is added to the basis set. This adds supplementary flexibility within the basis set, successfully permitting molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen. Likewise, d-type functions can be added to a basis set with valence p-orbitals and f-functions to a basis set with d-type orbitals and so on. The precise notation represents exactly which and how numerous functions are added to the basis set, such as (d,p).

Another typical addition to basis sets is the add-on value of diffuse functions, denoted by a plus sign(+). Two plus signs (++) represents that diffuse functions are also added to light atoms (hydrogen and helium). These extra basis functions can be significant when allowing for anions and other large and soft molecular system.

### 3.4.1 Minimal Basis Sets

A general naming convention for minimal basis set is STO-XG, where X is an integer. This X value indicates the number of Gaussian primitive functions comprising a single basis functions. The similar number of Gaussian primitives in the basis sets, comprises of core and valence orbitals. Minimal basis sets generally produce rough results that are inadequate for research quality publication, but are much cheaper than their larger equivalents. The most widely used minimal basis sets are:

- STO – 2G
- STO – 3G
- STO – 6G
- STO – 3G \*-polarized version of STO-3G

### 3.4.2 Split Valence Basis Sets

The initial way that a basis set can be made higher is to elevate the number of basis functions per atom. During most molecular bonding, it is the valence electrons, which chiefly take part in the bonding. In recognition of this fact, it is quite common to indicate valence orbitals by more than one basis function. The notation for these split-valence basis sets is typically X-YZG. In this case, X depicts the number of primitive Gaussians containing each core atomic orbital basis function. The Y and Z represent that the valence orbitals which are composed of two basis functions each, the first one composed of linear combination of Y primitive Gaussian functions, the other one is comprised of a linear combination of Z primitive Gaussian functions. In this case, the presence of two numbers after the hyphens depicts that this basis set is a split-valence double-zeta basis set. Split-valence triple- and quadruple-zeta basis sets are also known to offer as X-YZWG, X-YZWVG etc. The most generally used split-valence basis sets are:

- 3-21G
- 3-21G(d) or 3-21G\* - polarized
- 3-21G(d,p) or 3-21G\*\* - polarized
- 3-21+G – Diffuse functions
- 3-21+G\* or 3-21+G(d) - with polarization and diffuse function
- 4-21G
- 4-31G
- 6-21G
- 6-31G
- 6-31G\*
- 6-31+G\*
- 6-311G
- 6-311G\*
- 6-311G(d,p)
- 6-311+G(d) or 6-311+G\*
- 6-311++G(d,p)
- 6-31G(3df,3pd)

### 3.4.3 Double, Triple, Quadruple-Zeta Basis Sets

Basis sets in which there are several basis functions relating to each atomic orbital, such as both valance orbitals and core orbitals or just the valance orbitals, are known as double, triple and quadruple-zeta basis sets. Most commonly used multiple Zeta basis sets are:

- CC-PVDZ- Double –zeta
- CC-PVDZ-triple-zeta
- CC-PVQZ-quadruple-zeta
- CC-PVSZ-quintuple-zeta
- Aug-cc-pVDz- Augmented versions of the previous basis sets with additional diffuse functions.
- TZVPP-Valence triple-zeta plus polarization
- QZVPP-Valence quadruple -zeta plus polarization

The ‘CC-P’ at the commencement of some of the above basis sets stands for ‘correlation consistent polarised’ basis sets. They are double/triple/quadruple/quintuple-zeta for the valance orbitals and include consecutively larger shells of polarization (correlating) functions (d, f, g etc.) that can give convergence of the electronic energy to the entire basis set limit.

### 3.5 GAUSS VIEW

Gauss view is a cost effective, full-featured graphical user interface for Gaussian 09W. With the help of Gauss view, one can regulate input for submission to Gaussian and to examine graphically the output that Gaussian produces.

The initial step in producing a Gaussian input file is to build the desired molecule. The bond lengths, bond angles, and dihedral angles for the molecule will be used by Gauss view to write a molecular structure for the computation.

Gauss view incorporates a potential Molecule Builder. It can be used rapidly to sketch in molecules and analyze them in three dimensions. Molecules can be built by atom, ring, group, amino acid and nucleotide.

Gauss view is not incorporated with the computational module of Gaussian, but rather is a front-end/back-end processor to aid in the use of Gaussian. Gauss view can graphically exhibit an assorted range of Gaussian calculation results, including the following:

- Molecular orbitals
- Atomic charges
- Surfaces from the electron density, electrostatic potential, NMR shielding density, and other properties. It may also be displayed in solid, translucent and wire mesh modes.
- Surfaces can be tinted by a separate property.
- Animation of the normal modes with respect to vibrational frequencies.
- Animation of the steps in geometry optimizations, potential energy surface scans, intrinsic reaction coordinate (IRC) paths, and molecular dynamics trajectories from BOMD and ADMP calculations.

### **3.6 SCALING OF FORCE FIELDS**

SQM, the method of scaled quantum mechanical force fields (Pulay *et al.*, 1983) is a pragmatic approach to the Ab initio based evaluation of molecular force fields. Its initial idea is to use relatively low level Ab initio calculations using small basis sets and merge them with experimental information in the outline of an empirical adjustment, 'scaling' of the calculated force constants. SQM force fields are of comparable accuracy with the best purely theoretical results.

Quantum mechanical methods yield harmonic force constants. On the other hand, the observed frequencies are anharmonic, but it is promising to calculate the harmonic frequencies of small molecules from the observed vibrational spectra. The frequencies that are calculated on the basis of quantum mechanical force fields generally vary from the observed frequencies. This is partly due to the neglect of

anharmonicity and partly due to the estimated nature of the quantum mechanical methods. The scaling procedure fits the force field to observed (anharmonic) frequencies; therefore the scale factors are correct, in the anharmonicity. Thus, the reproduction of observed spectra may be enhanced with SQM force than with the best harmonic field.

The basic features of SQM are as follows:

(1) For the reference geometry, application of the theoretical geometry of the quantum chemical method, leads to the perfect choice and would be the best experimental geometry. This eliminates a major part of the shortcomings of the HF method in predicting potential surfaces (Fogarasi *et al.*, 1984). In practice, a dependable equilibrium structure is not always available and theoretical geometry is corrected based on the practice of tiny molecules.

(2) Scaling of force constants was proposed to account for the deviation of the calculated and the observed frequencies and was first attempted by Blom and Altona (1976). They scaled the diagonal internal force constants with different scale factors but used the same scale factors for the cross terms. Later on Pulay *et al.*, (1983) introduced a formula for the scaling of force constants  $f_{ij}$ :

$$f'_{ij} = \sqrt{S_i S_j} f_{ij} \quad (3.13)$$

where the symbol  $S_i$  and  $S_j$  expresses the scale factors for the diagonal force constants  $f_{ii}$  and  $f_{jj}$ . Pulay's method makes it possible to calculate scale factors that are transferable between similar molecules if suitable internal coordinates are chosen.

(3) For systematic calculations, the same basis set should be used consistently.

### 3.7 NORMAL COORDINATES ANALYSIS

A detailed explanation about vibrational modes can be best studied by means of normal coordinate analysis. It is a procedure for calculating the vibrational frequencies which correlates the observed frequencies of rather the harmonic infrared and Raman

frequencies to the equilibrium geometry, force constants and the atomic masses of the oscillating system. Normal coordinate analysis (NCA) has proven helpful in assigning vibrational spectra but its predictive ability widely depends on having consistent intra molecular force constants.

The issue related to the normal vibrations of a polyatomic molecule is satisfactorily dealt with, in particular, for small molecules by the method of classical mechanics. The frequency of a molecular vibration is examined by its kinetic and potential energies. The molecular vibrations are assumed to be simple harmonic. Analysis of molecular vibrations from classical mechanics will provide valuable information for the study of molecular vibrations by quantum mechanics because of the relationship between classical and quantum mechanics.

### 3.7.1 Number of Fundamentals in Each Symmetry Type

The number of vibrations of each type depends upon the geometry of the molecule. To find the number of fundamentals of each type a quantity  $\xi(R)$  for symmetry operations required  $\xi(R)$  is given by

$$\xi(R) = (U_R - 2)(1 + 2 \cos \varphi) \text{ For proper rotation} \quad (3.14)$$

$$\xi(R) = U_R (-1 + 2 \cos \varphi) \text{ For improper rotation} \quad (3.15)$$

Where,  $U_R$  is the number of nuclei unchanged by the symmetry operation. Knowing  $\xi(R)$  the number of each type is determined by using the relation (Albert cotton., 1990).

$$n_i = \frac{1}{g} \sum n_{\xi}^{\xi(R)} \chi_i \quad (3.16)$$

### 3.7.2 Removal of Redundant Coordinates

The number of internal coordinates must be equal to or greater than  $3N-6$  ( $3N-5$ ) degrees of vibrational freedom of molecule containing  $N$  atoms. If more than  $3N-6$

(3N–5) coordinates are chosen as the internal coordinates, which implies that these coordinates are independent of each other. In complex molecules, it is highly difficult to recognize a redundancy in advance. If an adequate number of internal coordinates is used, the number of redundancies can be created by subtracting 3N–6 (the number of internal degrees of freedom) from the number of internal coordinates. However, the essential internal coordinates may have been inadvertently omitted. If a molecule has symmetrical properties, these considerations can be applied separately to each species. The number of independent coordinates in each species can be severely obtained by reducing the representation formed by the Cartesian coordinates and subtracting the translations and rotations appropriately. The number of internal symmetry coordinates is similarly obtained for each species, and any excess depicts redundancy. One such general form of redundancies is also likely to occur in ring and these may involve the bond stretching coordinates as well as the bond angles. In the software developed for solving the vibrational secular equation, the redundant coordinates drop out as zero roots of the secular equation when the symmetrized kinetic energy matrix is diagonalized.

### 3.7.3 Framing the Secular Equations

Consider a molecule taking vibrational motion and let there be several number of normal modes of vibration. The centre of gravity of the molecules in its equilibrium configuration may be chosen as the origin of the coordinate system so as to express the displacement in each normal vibration in terms of Cartesian coordinates. The total kinetic energy is given by the formula,

$$2T = \sum_{i=1}^n m_i \left( X_i^2 + Y_i^2 + Z_i^2 \right) \quad (3.17)$$

This equation can be simplified by using a new set of Cartesian coordinates referred as the reduced displacement coordinates,

$$q_1 = \sqrt{m_1} X_1, \quad q_2 = \sqrt{m_2} X_2, \quad q_3 = \sqrt{m_3} X_3, \quad q_4 = \sqrt{m_4} X_4, \dots \quad (3.18)$$

Now the equation 3.17, can be written as

$$2T = \sum_{i=1}^n a_{ij} q_i q_j \quad (3.19)$$

If the vibrations are simple harmonic, then the potential energy in lower coordinates, can be written as

$$2V = \sum_{i,j}^{3n} b_{ij} q_i q_j \quad (3.20)$$

The  $b_{ij}$  values are constants and the  $a_{ij}$  values are functions of the atomic masses,  $q_i$  and  $q_j$  are the  $i^{\text{th}}$  and  $j^{\text{th}}$  coordinates.

The classical equation of motion for the  $i^{\text{th}}$  mass by using the Newton's equation in the Lagrange form is:

$$\frac{\delta}{\delta t} \left( \frac{\delta T}{\delta q_i} \right) + \frac{\delta V}{\delta q_i} = 0 \quad (3.21)$$

Using equations 3.19 and 3.20 in 3.21 we get

$$\sum_i \left( a_{ij} q_j + b_{ij} q_j \right) = 0 \quad (3.22)$$

The general solutions of the above equation is given by

$$q_i = A_j \sin(\lambda^{1/2} t + \varphi) \quad (3.23)$$

Which is an equation characteristic of wave motion with  $\lambda = 4\pi^2\nu^2$  where  $\nu$  is the frequency, and  $A$  and  $\varphi$  are amplitude and phase constant, respectively. From equations 3.22 and 3.23

$$\sum_{i=1}^{3n} (b_{ij} - a_{ij}\lambda) A_j = 0 \quad (3.24)$$

Where,  $j=1,2,3,\dots,3n$ . For non-trivial solution the determinant of the coefficients must be equal to zero i.e.,

$$|b_{ij} - a_{ij}\lambda| = 0 \quad (3.25)$$

The above equation 3.25 is referred as the secular determinant. It has  $3n$  roots,  $\lambda_i$  for which the above equation is satisfied. Each of these  $\lambda$  values expresses the harmonic vibration of a mass particle with frequency  $\nu$ . These  $\nu$  values are the normal frequencies of the vibrations. The values of  $\lambda$  can be substituted back in equation 3.24 and  $A_j$  can be calculated which will imply the vibration (Barrow, 1964).

### 3.7.4 Evaluation of the Secular Determinant

The evaluation of the secular determinant is further simplified by the transformation to a new set of coordinates  $Q_i$ , such that the cross product terms in 3.19 and 3.20 fades away. The old and new coordinates can be correlated by an orthogonal transformation,

$$q_k = \sum_{i=1}^{3n} B_{ki} Q_i \quad (3.26)$$

The coordinates  $Q_i$  are known as the normal coordinates for the molecular system. Based on the equation 3.14 and 3.15, the kinetic and potential energies can be written as

$$2T = \sum_i Q_i^2 \quad (3.27)$$

$$2V = \sum_i \lambda_i Q_i^2 \quad (3.28)$$

Employing equations 3.26 and 3.27 in 3.21, we get,

$$\square Q_i + \lambda_i Q_i = 0 \quad (3.29)$$

The solution of this expression is given

$$Q_i = B_i \sin(\lambda_i^{1/2} t + \varphi) \quad (3.30)$$

The vibrational problem is much more easier to represent by means of matrix algebra. Thus, the expression for kinetic and potential energies in matrix notation is

$$2T = Q^T Q \quad (3.31)$$

and

$$2V = Q^T \Lambda Q \quad (3.32)$$

Where  $\Lambda$  is the diagonal matrix with element  $\lambda_i$  and  $Q^T$  depicts the transpose of the column matrix  $Q$  of the normal coordinates. The simplified forms of the secular equation can now be written as,

$$|\Lambda - E\lambda| = 0 \quad (3.33)$$

This equation will have  $3N-6$  roots  $\lambda_i$  and each value of  $\lambda$  corresponding to a normal vibrational frequency of the molecule. All the atoms vibrate with the identical frequency and phase in each normal mode  $Q_i$  (Sathyanarayana, 2004).

### 3.7.5 Solution of Secular Equation in Internal Coordinates

If internal coordinates are used as the initial coordinates the solution of the secular determinant 3.33 is simplified. The internal coordinates are referred as the increments in bond lengths and bond angles. The main advantage of internal coordinates is the implementation of the possible potential energy or force constant matrix in terms of bond stiffness and resistance to bond angle determinations, which make these coordinates physically comprehensible. The size of the secular equation in internal coordinates is highly similar and hence easier to solve.

The kinetic energy in terms of internal coordinates is given by the expression

$$2V = \sum_{ij} G_{ij}^{-1} r_i r_j \quad (3.34)$$

Where,  $G_{ij}^{-1}$  is the inverse kinetic energy elements for each pair of coordinates  $r_i$  and  $r_j$ .

Similarly, the potential energy in internal coordinates is

$$2V = \sum_{ij} f_{ij} r_i r_j \quad (3.35)$$

Where,  $f_{ij}$  is the harmonic force constants.

In matrix notation, the equation 3.34 and 3.35 can be suitably expressed by the equation

$$2T = R G^{-1} R \quad (3.36)$$

and

$$2V = R^T F R \quad (3.37)$$

Where  $G^{-1}$  is the inverse kinetic energy matrix and  $F$  is the potential energy matrix comprises of the intermolecular force constants. Using equations 3.36 and 3.37 in the Newton's equation in Lagrange form given by equation 3.21 and simplifying, we get the secular determinant as

$$|GF - E\lambda| = 0 \quad (3.38)$$

Where,  $E$  is the unit matrix. The expression 3.38 expresses the secular equation by involving the product term  $GF$ . This method of expressing the secular equation was first explained by Wilson and so it is often referred as Wilson's  $FG$  matrix method (Wilson *et al.*, 1955).

In order to frame a secular equation 3.38 for a polyatomic molecule it is mandatory to select appropriate set of internal coordinates and then set up the  $F$  and  $G$  matrix. At least  $3N-6$  internal coordinates are required to describe the vibration of an  $n$ -atom molecule. Sometimes, it is necessary to include more than  $3N-6$  internal coordinates and this will consequently leads to redundancies. These redundancies (interdependence of internal coordinates) can be eliminated later under appropriate coordinate transformation.

### 3.7.6 Solution of Secular Equation in Symmetry Coordinates

After setting up the  $F$  and  $G$  matrix, the secular determinant 3.38 can be solved for eigen values and eigen vectors. But the size of the determinant is very high for most of the polyatomic molecules. It is used to minimize the order of the determinant by taking advantage of the molecular symmetry. The generalization can be effected by the use of symmetry coordinates (Ross., 1972) and they are simple linear combinations of internal coordinates. For introducing symmetry coordinates, the initial step is to classify the normal vibrations according to the irreducible representation of the point group to which the molecule belongs. The symmetry coordinates are next selected so as to transform according to the complete irreducible representations of the molecular point group. These coordinates blocks the diagnosis the secular determinant. Hence, the problem of solving the determinant of the order  $3N-6$  is minimized to the problem of solving several independent determinants of smaller order (Barrow., 1964).

By using an orthogonal coordinate transformation internal coordinates  $R$  can be converted to symmetry coordinates  $S$  and such an operation is represented as,

$$S = UR \quad (3.39)$$

Where,  $U$  is an orthogonal matrix. The  $G$  and  $F$  matrices in internal coordinates can be block-diagonalised using the  $U$ -matrix as b

$$UGU^T = G_s \quad (3.40)$$

$$UFU^T = F_s \quad (3.41)$$

The above equations yield  $G$  and  $F$  matrices in symmetry coordinates. Now, the secular determinant in terms of symmetry coordinates is,

$$|G_s F_s - E\lambda| = 0 \quad (3.42)$$

This expression has the similar roots as the secular equation 3.38 in terms of internal coordinates and thus the eigen values and eigen vectors of both 3.42 and 3.38 are similar.

When the eigen values  $\lambda$  are determinant, the given vectors  $L$  for each of the eigen values can be analyzed from

$$|G_s F_s - E\lambda| L = 0 \quad (3.43)$$

### 3.7.7 Potential Energy Distribution

In the normal analysis, potential energy distribution (PED) plays a key significant role in obtaining a thorough understanding about the nature of the normal modes. The PED is articulated in terms of the percentage contribution of each force constant or the displacement coordinates or symmetry coordinate to the potential energy of each normal mode.

The normal coordinates ( $R_i$ ) are correlated to the normal coordinates ( $Q_k$ ) as follows-

$$R_i = \sum_{k=1}^{3n-6} L_{ik} Q_k \quad (3.44)$$

Where,  $L_{ik}$  is the component of the L-matrix. Substitution of equation 3.44 to the potential energy expression 3.30 gives the potential energy of the molecule, for a vibration of frequency  $\nu_k$  linked with a normal coordinates  $Q_k$ ,

$$2V = Q_k^2 \sum_{ij} f_{ij} L_{ik} L_{jk} \quad (3.45)$$

Such terms are large only when  $i=j$ , since the diagonal force constants  $f_{ij}$  are much higher than the off-diagonal constants  $f_{ij}$ . Consequently, to get the PED, only the terms  $f_{ii}L_{ik}^2$  required to be calculated. The normalization condition  $L^T fL = \Lambda$ , gives the relation of the form

$$\sum_{ij} f_{ij} L_{ik} L_{jk} = \lambda_k \quad (3.46)$$

Neglecting the cross terms yields,

$$\sum_i f_{ij} L_{ik}^2 = \lambda_k \quad (3.47)$$

The potential energy has to be calculated in the current investigation using the relation

$$PED = \frac{F_{ii} L_{ik}^2}{\lambda_k} \quad (3.48)$$

Where  $F_{ii}$  is the potential energy constant,  $L_{ik}$  is the L matrix element and  $\lambda_k$  is equal to  $4\pi^2 c^2 \nu_k^2$ .

It is the involvement of the  $i^{th}$  symmetry coordinates to the potential energy of the vibration whose frequency is  $\nu_k$  (Shimanouchi., 1962). The input of the potential energy from the individual diagonal elements gives an increase to a conceptual link between the empirical analysis of the vibration spectra of complex molecules dealing with the characteristics group frequencies and the theoretical approach from the computation of the normal modes.

### 3.8 SCALING OF AB INITIO FORCE FIELDS BY MOLVIB

Normal coordinate analysis (NCA) is nowadays generally employed as an aid in the interpretation of the vibrational spectra of large molecules. In order to get meaningful results, knowledge of vibrational force field is required. Since the number of force constants grows quadratically with the number of atoms, one has to take up

many approximations in the calculation of harmonic force field even for moderately large molecules. To overcome this difficulty, one can evaluate a force field for a set of related molecules using the overlay method introduced by Schacht Schneider and Snyder in the 1960. Gwinn introduced a programme for NCA using mass-weighted Cartesian coordinates (Gwinn., 1977), which removes the redundancy problems arising when internal valance coordinates are used as in Wilson's FG-method. MOLVIB (Sundius., 1980; 1990), a FORTRAN programme is based on the above idea developed for the calculation of harmonic force fields and vibrational modes of molecules with upto 30 atoms. All the calculations are done in terms of mass weighted Cartesian coordinates, instead of internal coordinates as in the conventional FG-method. This makes it possible to overcome the issues with redundant coordinates. The force field is refined by a modified least squares fit for the observed normal frequencies.

MOLVIB can be best utilized for the scaling of vibrational force fields by treating the scale factors as ordinary force constants. Thus, they can be calculated from a least squares fit for the calculated and observed frequencies (Sundius, 2002). To perform the scale factor calculations, the programme requires the atomic coordinates, and the Cartesian force constants from an abinitio calculation. An auxiliary programme (Rdarch) is used to take out these data from the archive part of the out file of ab initio calculations. In addition, this programme can also extract the dipole derivatives and the polarization derivatives, which are required for intensity calculations. MOLVIB will transform the Gaussian force constants, which are represented in atomic units into the units used by the programme. Since the optimal values of the scale factors generally less than 1, is good to start with an initial calculation, where all the scale factors have been set to 1, and check that MOLVIB can duplicate the frequencies calculated by the abinitio programme.

There are three different methods available for the scale factor calculations in MOLIVB. In two of these methods, the non diagonal terms in the potential energy will surely depend on non-linear scale factors as,

$$2V = \sum_i \hat{a}_i S_i f_{ij} q_i q_j + \sum_i \hat{a}_i \sum_{j' \neq i} \hat{a}_{j'} \sqrt{S_i S_{j'} f_{ij} f_{i'j'}} q_i q_{j'} \quad (3.49)$$

The factor  $\sqrt{S_i S_j}$  that takes place in front of the non diagonal force constant has to be repeated. The frequency fit generally converges in four or five iterations, and often just a few repetitions are necessary. The values for the scale factors initially are placed to 1.

It is also probable to utilize individual scale factors for the non diagonal force constants. In this case, scale factors should be linked both with diagonal and non diagonal terms. Similar ideas have been proposed by Blom and Altona (1976). However, too many diverse scale factors should not be used in this case, but instead group identical factors together, tend to make the total number of scale factors which must be very low. The scale factors are computed from a least square fit of the observed vibrations in a identical way as the force constants.

### 3.9 NATURAL BOND ORBITAL (NBO) ANALYSIS

Natural bond orbital (NBO) analysis (Foster and Weinhold., 1980) was developed as a technique for analyzing hybridization and covalency effects in polyatomic wave functions. The work of Foster and Weinhold was extended by Reed *et al.*, (1985) who employed NBO analysis that exhibited specifically H-bonded and other strongly bound Vander Waals complexes (Reed *et al.*, 1988). Ab initio wave functions that are converted to NBO form are found to be in good agreement with Lewis structure concepts and with the basic Pauling-Slater-Coulson picture (1931) of bond hybridization and polarization. The filled NBOs  $\sigma$  of the “natural Lewis structure” is well adapted to explain the covalency effects in molecules (Reed *et al.*, 1988). Moreover, the common conversion to NBOs also results in orbitals that are unoccupied in the formal Lewis structure and that may be utilized to describe non-covalent effects. The symbols  $\sigma$  and  $\sigma^*$  are utilized in a generic sense to refer to filled and unfilled orbitals of the formal Lewis structure, through the formal orbital may actually be core orbitals (C), lone pair (n),  $\sigma$  or  $\pi$  bonds ( $\sigma$ ,  $\pi$ ), and so forth, and the latter may be  $\sigma$  or  $\pi$  anti bonds ( $\sigma^*$ ,  $\pi^*$ ), extra valence shell Rydberg (r) orbitals, and present according to the particular case.

The anti bonds depicts unused valence-shell capacity, spanning portions of the valence space that are usually unsaturated by covalent bond formation. The non-covalent delocalization effects are linked with  $\sigma \rightarrow \sigma^*$  interactions between filled (donor) and unfilled (acceptor) orbitals, it is quite natural to explain them as being of “donor-acceptor”, charge transfer, or generalized “Lewis base-Lewis acid” type. NBO calculations (Chocholousova., 2004) were performed using NBO 3.1 program (Glendening *et al.*, 1988) as implemented in the Gaussian 09W package (Frisch *et al.*, 2008) at the HF and DFT methods with basis sets.

### 3.9.1 Second-order Perturbation Theory Analysis

The second-order perturbative estimates the donor-acceptor (bond-antibond) interactions in the NBO analysis. The second-order Fock matrix was used to evaluate the donor-acceptor interactions in the NBO basis (Szafran, 2007). The interactions impact in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor NBO ( $i$ ) and acceptor NBO ( $j$ ), the stabilization energy  $E(2)$  correlated with delocalization ("2e-stabilization")  $i \rightarrow j$  is just estimated as

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \quad (3.50)$$

Where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$ ,  $\varepsilon_j$  are diagonal elements (orbital energies) and  $F(i,j)$  is the off-diagonal NBO is the Fock matrix element.

The localized orbitals in the Lewis structure can interact with high affinity. A filled bonding or lone pair orbital can act as a donor and blank or filled bonding, anti bonding, or lone pair orbital can act as an acceptor. These interactions can highly strengthen and weaken bonds. For example, a lone pair donor anti bonding acceptor orbital interaction will weaken the bond linked with the antibonding orbital. Conversely, an interaction with a bonding pair as the acceptor will reinforce the bond. A well-built electron delocalization in Lewis structure will also explain up as donor-acceptor interactions.

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## 3.10 OTHER MOLECULAR PROPERTIES

### 3.10.1 Non-Linear Optical (NLO) Properties

The improvement of organic non-linear optical (NLO) materials for device application requires a multi disciplinary effort relating both theoretical and experimental studies in the fields of physics, chemistry and engineering. Quantum chemical calculations (QCC) have created a significant input to the understanding of the electronic population underlying the molecular NLO processes and the structure-property relationships (Prasad and Williams., 1991; Meyer., 1994). The most consistent structure property relationships, is where the property describes the linear polarizability ( $\alpha$ ) and first polarizability ( $\beta$ ) that are required for the rational design of optimized materials for photonic devices such electro optic modulators and all optical switches.

Non-linearity in organic chromophores is synthetically modified by differing in the composition or length of conjugated  $\pi$ -systems and by describing the results of varied electron-donor and acceptors. However, the richness or deficiency of electron in the aromatic rings cannot be foreseen on the premise of the calculated ring atom charge densities as these quantities are highly susceptible to the standard of the premise sets employed. Since the NLO properties depend on the extend of charge transfer (CT) interaction across the conjugative paths and the electron transfer capacity of an aromatic ring depends primarily on its ionization potential(IP) and electron affinity (EA) which, in the framework of MO theory and Koopman's theorem respectively.

NLO processes can be described as dielectric phenomena. Electric field such as an applied dc field or propagating electromagnetic waves when passes through the medium forces electrons displacement. Electrons that are bound to the nearest nuclei in the medium gets slightly perturbed by the external applied electromagnetic field and starts oscillating at the applied frequency. The magnitude of such an induced polarization (P) at modest field strengths will be proportional to the applied field and represented as,

$$P = \chi_1^{(1)} E \quad (3.51)$$

Where  $E$  is the magnitude of the applied electric field and  $X^{(l)}$  is the polarizability of the material.

The NLO phenomenon takes place at sufficiently intense fields. As the applied field strength elevates (e.g., lasers) the polarization response of the medium is no longer linear as shown by the (3.51). The induced polarization ( $\chi^x$ ) becomes a function of the applied field and given-

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots \quad (3.52)$$

Where the  $\chi^{(2)}$  and  $\chi^{(3)}$  coefficients express the second and third order susceptibilities of the medium respectively.

At the molecular level eq. (3.52) is represented as

$$P = \sum \alpha_{ij}E + \sum \beta_{ijk}E^2 + \sum \gamma_{ijkl}E^3 + \dots \quad (3.53)$$

Where  $\alpha_{ij}$ —polarizability,  $\beta_{ijk}$ —first hyperpolarizability (second order effects),  $\gamma_{ijkl}$ —Second hyperpolarizability (third order effects) and  $i,j,k,l$  corresponds to the molecular coordinates.

A medium exhibiting such a non-linear optical response might contains of a crystal compound of molecules with asymmetric charge distribution. If the medium (or molecule) is centrosymmetric, then first order hyperpolarizability ( $\beta$ ) is ordinal, representing that centrosymmetric media do not show second harmonic generation. This can be explained as follows. If a field  $+E$  is applied to the medium, eq. (3.54) that predicts the first nonlinear term as  $+\beta E^2$ . If a field  $-E$  is applied, the polarization is still predicted to be  $+\beta E^2$ . Yet if the medium centrosymmetric the polarization should be  $-\beta E^2$ . This contradiction can be resolved only if  $\beta=0$ . Thus the centrosymmetric medium has zero  $\beta$  value. In case of third order NLO susceptibility, if  $+E$  field gives polarization  $+\gamma E^3$  and  $-E$  field produces  $-\gamma E^3$ , so the second order hyperpolarizability ( $\gamma$ ) is the first non-zero nonlinear term in centrosymmetric media.

### 3.10.2 Natural Population Analysis

The natural population analysis (NPA) method proposed by Weinhold *et al.*, (Reed *et al.*, 1985) is recently budding as a authoritative alternative to the extensively used Mulliken population analysis (Mulliken, 1995) for interpretation of the results of quantum chemical calculations. Certainly, a method of “natural population analysis” has been residential to compute atomic charges and orbital populations of molecular wave functions in common atomic orbital basis sets. The general analysis is the alternative to conventional Mulliken population analysis, and found to have empowered with numerical stability and to better portray the electron distribution in compounds of elevated ionic character, such as those having metal atoms. We calculated ab initio SCF-MO wave functions for compounds of types  $\text{CH}_3\text{X}$  and  $\text{LiX}$  ( $\text{X}=\text{F}, \text{OH}, \text{NH}_2, \text{CH}_3, \text{BH}_2, \text{BeH}, \text{Li}, \text{H}$ ) in a diverse range of basis sets to exemplify the generality of the method, and to compare the natural populations with results of Mulliken analysis, density integration, and empirical measures of ionic character. Native populations yield an inexpensive description of those molecules, providing a unified treatment of valence and extreme ionic limits at modest science value.

The analysis of the electron density distribution inside a molecular system is supported by the orthonormal natural atomic orbitals. Natural populations,  $n_i(\text{A})$  are the best places of the general atomic orbitals. This will rigorously satisfy the Pauli exclusion principle:  $0 < n_i(\text{A}) < 2$  The population of an atom  $n(\text{A})$  is the total sum of natural populations  $n(\text{A}) = \sum_{\text{A}} n_i(\text{A})$ . A distinguished feature of the NPA method is that it widely resolves the precise set dependence problem that is gone downside in the Mulliken population analysis method.

### 3.10.3 HOMO and LUMO Analysis

Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO) are called the frontier orbitals and determine the way, the molecule interacts with other species. The HOMO is the major orbital that acts as an electron donor, since it is the outermost (highest energy) orbital comprising of electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost

(lowest energy) orbital that has room to accept electrons. In accordance with the above definitions, a single orbital may be both the LUMO and the HOMO. The molecular orbital (MO) is delocalized over many atoms. The  $\sigma$  (or  $\sigma^*$ ) type molecular orbitals are usually separated from  $\pi$  (or  $\pi^*$ ) type MOs. One exception is that will be discussed by us which is known as hyperconjugation. The HOMO correspond to a filled  $\pi$ -type orbital or a lone pair (nonbonding electrons), and the LUMO corresponds to an empty atomic p,  $\pi^*$ -type orbital or to an empty  $\sigma^*$  orbital.

### 3.10.4 Reactivity Descriptors

Some of the chemical phenomena is understood and expected by some theoretical quantities that have a right away relationship with the characteristic sets of important chemical properties. These quantities are in generally called descriptors. The global descriptors of hardness have been a pin pointer of general stability of the system. The constraint hardness is also interpreted as the struggle made by the chemical potential to alter in the number of electrons or resistance to deformation or change. The reduced worth of hardness is ordinal and it corresponds to the greatest softness. Since these parameters (chemical potential, hardness and softness) are obtained by averaging over atomic or molecular space, these are called global reactivity descriptors. The density based descriptors are known to play key role in determining the stability and reactivity of chemical species. There have been recent studies on the qualitative and quantitative descriptors of these concepts and use of these in the selectivity of reactions in catalysis, adsorption and molecular recognition. Global reactivity descriptors (GRD), like softness, hardness and chemical potential along with concept of hard soft base (HSB) principle are widely used in describing the reactivity and the stability of chemical systems (Becke., 1993). On the other hand, local reactivity descriptors (LRD), e.g. Fukui function (FF), local softness (Proft and Greerlings., 2002) etc. have been studied extensively in recent years for characterizing the reactivity and site-selectivity in chemical reaction. These descriptors have been used qualitatively to characterize reactivity of a molecule in chemical reaction. Reactivity to specific agents e.g. electrophilic, nucleophilic or radical can be described qualitatively using the above descriptors (Proft and Greerlings, 2002).

To describe these reactivity descriptors for atoms in a molecule, condensed definitions of electrophilicity, nucleophilicity etc. have been proposed using electronic population of an atom (Yong and Mortier, 1986). These condensed local descriptors have also been used to study the site-selectivity in a chemical reaction (Proft and Greerlings, 2002). Among different population analysis (Lowdin., 1953), Parr *et al.*, (1999) have shown that the Hrishfeld analysis provides correct non-negative values of FF. Recently, relative electrophilicity and relative nucleophilicity, which are ratios of electrophilic to nucleophilic FF and vice-versa respectively, have been identified as more reliable criteria for intra-molecular reactivity (Roy *et al.*, 1998). More recently, Parr *et al.*, have defined a new concept of global philicity (Parr *et al.*, 1999) from which Chattaraj *et al.*, (2003) have defined local philicity and indices which have been the subjects of recent study.

### **3.11 THERMODYNAMIC PROPERTIES**

Thermodynamics are usually relevant to a diverse difference of topics in science and engineering, like engines, part transitions, chemical reactions, transport phenomena, and even black holes.

#### **3.11.1 Heat capacity (C)**

Heat capacity generally denoted by a capital C, typically with subscripts, or thermal capability, is that the measurable physical quantity that influences the number of warmth necessary to alter a substance. Derived quantities that specify heat capacity as an intensive property, i.e., independent of the size of a sample, are the molar heat capacity, which is the heat capacity per mole of a pure substance, and the specific heat capacity, often basically called specific heat, which is the heat capacity per unit mass of a material. Heat capacities of materials have the capacity to quantify atoms or particles they enclose, intensive heat capacities of assorted substances that are articulated directly or indirectly per particle tend to diverge within a much more narrow range.

### 3.11.2 Entropy (S)

Entropy is a thermodynamic property that is the appraise of a system's thermal energy per unit temperature that is unoccupied for doing useful work. Perhaps, the most popular demonstration of entropy is that, subsequent the laws of thermodynamics, entropy of a closed system always elevates and in heat transfer reactions, heat energy is transferred from elevated temperature components to minimal temperature components. Entropy runs in a single direction only in thermally isolated systems. One can estimate the entropy of a system to decide the energy that is not available for work in a thermodynamic process, such as energy conversion, engines, or machines. Such processes and devices can only be driven by adaptable energy, and have a theoretical improved efficiency when converting energy to work. During this point of work, entropy stays in the system, which then liberates in the form of waste heat.

### 3.11.3 Enthalpy (H)

Enthalpy is a total measure of the energy of a thermodynamic system. It includes the internal energy, which is the energy needed to create a system, and the amount of energy needed to make room for it by displacing its environment and establishing its volume and pressure. Enthalpy is a thermodynamic potential and regarded as the state function and widespread in the amount.

The enthalpy is the selected expression of system in which the energy alters in numerous chemical, physical and biological measurements, since it simplify certain implications of energy transfer. This is because, alteration in enthalpy takes account of energy transferred to the environment through the expansion of the system under study. The total enthalpy, H, of a system cannot be calculated directly.

### 3.11.4 Gibbs Free Energy (G)

The Gibbs free energy is defined as the thermodynamic potential that energies the "potential" or process-initiating work that are available from a thermodynamic system at a constant temperature and pressure in thermodynamics. Just as in mechanics, where potential energy is expressed as the capacity to do work, likewise diverse

potential have diverse meaning. The Gibbs free energy is the highest amount of non-expansion work that can be extracted from a closed system; this highest value can be achieved only in a completely reversible process. When a system differs from a well-defined initial state to a well-defined final state, the Gibbs free energy  $G$  contemplates with the work exchanged by the system with its surroundings, minus the work of the pressure forces, in a reversible transformation of the system from the similar initial state to the final state. Gibbs energy is also known for the chemical potential that is reduced when a system attains equilibrium at stable pressure and temperature.

### **3.11.5 Zero-Point Vibrational Energy (ZPVE)**

Zero-point energy (ZPE) or zero-point vibrational energy (ZPVE) is the minimum possible energy that a quantum mechanical physical system may have; it is the energy of its ground state. All quantum mechanical systems experience fluctuations even in their ground state and have linked zero-point energy, an impact of their wave-like nature. The uncertainty principle requires every physical system to have a ZPE greater than the minimum of its classical potential well, is present even at absolute zero. For example, liquid helium does not freeze under atmospheric pressure at any temperature because of its ZPE. A related term is zero-point field, which is the minimum energy state of a specific field.