2.1. Introduction

Quantum chemical computational methods have become a useful tool for solving interesting chemical problems and reaction mechanism. It has become a useful way to investigate materials to make predictions about the structure and properties of molecule and solids before running the actual experiments that are too difficult or too expensive [1]. Due to Ultrafast developments in computer hardware and associated achievements, quantum chemical methods can now be directly applied for various scientific applications.

Computational quantum studies use the results of theoretical chemistry and they are incorporated into efficient computer programs to calculate the structure and properties of the compound chosen, which normally complement the information obtained by chemical experiments. It is widely used in the design of new drugs and materials. The properties such as influence on structure (i.e. the expected positions of the constituent atoms), absolute and relative (interaction) energies, vibrational frequencies, dipoles and higher multipole moments, electronic charge, reactivity and other spectroscopic quantities can be evaluated [2,3].

The calculations are based primarily on Schrodinger's equation and include:

- geometry optimizations
- frequency calculations
- interpretation of experimental data
- Potential energy surfaces (PES)
- Frontier molecular orbital analysis
- Natural bond orbital analysis
- transition structures
- electronic structure determinations
- rate constants for chemical reactions (kinetics)
- electron and charge distributions
thermodynamic calculations – heat of reactions, energy of activation and particularly useful for determination of properties that are inaccessible experimentally

Quantum mechanically derived harmonic force fields are widely used at present for the calculation of frequencies and the normal mode of vibrations. Nowadays, the increasingly available sophisticated electron correlation calculations deliver force fields of high accuracy for small polyatomics. The scaled quantum mechanical (SQM) force fields [4,5] are of comparable accuracy with the theoretical results. In addition, the scaling procedure fits the SQM force field to observed frequencies. Thus, the reproduced observed spectra will be better with SQM force field than with the harmonic field.

2.1.1. Energy minimization

The quality of the force field calculation depends on the appropriate energy expression and the accurate geometrical parameters. The potential energy calculated by summing up the energies of various interactions is a numerical value for a single conformation. The geometries and relative energies must be optimized for energy minimization. Energy minimization is usually performed by gradient optimization i.e., the atoms are allowed to move in order to reduce the net force on them. The energy minimized structure serves as an excellent starting point for molecular dynamics simulations since it has small forces on each atom.

Molecular mechanics deals with the changes in the electronic energy of the molecule due to bond stretching ($v_b$), in-plane bending ($v_\theta$), out-of-plane bending ($v_{o\theta}$), internal rotation (torsion) about bonds ($v_\phi$), Van der Waals attractions and repulsion between non-bonded atoms ($v_{dw}$), interactions between different kinds of motions ($v_{int}$) and electrostatic interactions between atoms ($v_{es}$). The sum of these contributions give the potential energy $V$ for the motion of the atoms in the molecule. It is known as the steric energy or strain energy for the motion of atoms in the molecules.

The mathematical form of this energy function (also called potential energy surface) is given below:

$$V(x^N) = \sum_{i=1}^{k} v_i$$  \hspace{1cm} .......(2.1)
Where V represents the potential energy of the molecular system, which is a function of the Cartesian coordinates of all atoms denoted as \( X^N \). The equation (2.1) can be written as,

\[
V = v_b + v_\theta + v_\Phi + v_{es} + v_{dw} + v_{int} \quad \ldots \quad (2.2)
\]

The potential energy calculated by summing up the energies of various interactions is a numerical value for a single conformation. The geometry optimization starts with the initially assumed geometry and by minimizing the steric energy \( V \) of the equation (2.2) the nearest local energy minimum will be found. This equation provides an analytical form for the energy, the first and second derivatives of \( V \) can easily be evaluated analytically, which facilitates the energy minimization. Many low energy conformers for a molecule will be predicted by the built-in searching methods available in many molecular optimization programs. Force field methods are primarily geared to predict geometries and relative energies.

2.2. Computational Chemistry

Computational chemistry simulates chemical structures and reactions numerically, based on full or on part of the fundamental laws of physics. Quantum chemical calculations are today performed on a wide range of molecules using advanced computer programs. Today quantum chemical calculations are an important complement to many experimental investigations in organic, inorganic and physical chemistry as well as to atomic and molecular physics.

There are two broad areas within computational chemistry: molecular mechanics and electronic structure theory. They both perform the following basic type of calculation.

- Computing the energy of a particular molecular structure (physical arrangement of atoms or nuclei and electrons).
- Performing geometry optimizations, which locate the lowest energy molecular structure in close proximity to the specified starting structure. Geometry optimizations depend primarily on the gradient of the energy – the first derivative of the energy with respect to atomic positions.
- Computing the vibrational frequencies of molecules resulting from interatomic motion within the molecule. Frequencies depend on the second derivative of the energy with respect to atomic structure and frequency calculations may also predict other properties,
frequency calculations are not possible or practical for all computational chemistry methods.

### 2.3. Ab initio methods

Ab initio orbital molecular methods are useful to predict harmonic force constants and normal modes of frequencies. The ab initio methods first optimize the molecular geometry and then evaluate the second derivatives at the equilibrium positions usually using analytical derivatives. Such methods provide reliable values for harmonic vibrational frequencies for fairly large sized molecules. Additionally, such calculations can be used to predict barriers to internal rotation as well as relative stabilities of different conformers. The information obtained from structural parameters, conformational stabilities, force constants, vibrational frequencies as well as infrared and Raman band intensities has given significant contributions to the field of vibrational spectroscopy.

Harmonic force constants in Cartesian coordinates can be directly derived from ab initio calculations. These force constants can be transformed to internal or symmetry coordinates. To make reliable vibrational assignments to most of the fundamentals, ab initio calculations followed by normal coordinate analysis are very helpful. Band intensities from ab initio studies are another important output which also helps in making vibrational assignments. Hartree-Fock method and Density Functional Theory (DFT) are the two principally different quantum mechanical methods addressing the vibrational problems. Density functional calculation has emerged in the past few years as successful alternative to traditional Hartree-Fock method. For determining the electronic structure of molecules, the DFT methods, particularly hybrid functional methods [6-9] have evolved as powerful quantum chemical tool. In the framework of DFT approach, different exchange and correlation functional are routinely used. Among these, the Becke-3-Lee-Yang-Parr (B3LYP) combination [10,11] is the most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and various standard basis sets, provide an excellent compromise of vibrational spectra for medium and large size molecules. The vibrational frequencies calculated by applying DFT methods are normally overestimated than experimental values by 2-5% on an average due to the neglect of electron correlation, anharmonicities and incomplete basis sets.
This overestimation can be narrowed down by empirical scaling done using scale factors ranging from 0.8 to 1.0. These scale factors depend both on method and basis sets and they partially compensate for the systematic errors in the calculation of frequencies. Some scaling methods advocated to minimize the overestimation of the frequency differences are uniform scaling and selective scaling or multiple scaling. Ab initio calculation could be performed using GAUSSIAN 09 Software package [12].

If the quantum-mechanical force field is not corrected, especially in the case of large deviations from the experimental results, this omission can complicate the theoretical analysis of the vibrational spectrum of a molecule and can lead to errors in the assignment of the experimental frequencies. Therefore, determining empirical corrections to quantum mechanical force fields is important. It is shown that among all the methods for empirically correcting quantum–mechanical force fields, the one with the best physical basis is the modern version of the Pulay method [13-14].

A simple flow chart, which explains the complete scheme of calculation by quantum chemical methods, is given below in Figure 2.1.

Figure 2.1. Flow diagram of program used in the quantum chemical calculations
2.4. Density Functional Theory

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

Traditional methods in electronic structure theory, in particular Hartree-Fock 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 function with the electronic density as the basic quantity. Whereas the many-body wave function 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 conceptually 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-Kohn theorems [15]. The first theorem demonstrates the existence 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 minimizes the total electronic energy of the system. The most common implementation of density functional theory is through the Kohn-Sham method. Within the framework of Kohn-Sham DFT, the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the coulomb interactions between the electrons, eg. the exchange and correlation interactions.

2.4.1. Derivation and formalism of DFT

As usual in many body electronic structure calculations, the nuclei of the treated molecules are seen as fixed, generating a static external potential $V$ in which the electrons are moving. A stationary electronic state is then described by wave function $\Psi(r_1,...,r_n)$ fulfilling the many-electron Schrödinger equation.

$$H\Psi = [T + V + u]\Psi = \left[ \sum_{i} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i} V(r_i) + \sum_{i<j} U\left(r_i, r_j\right) \right] \Psi = e\Psi \quad \ldots \ldots (2.3)$$
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 called universal operators as they are the same for any system, \( V \) is system dependent or non-universal. The actual difference between a single-particle problem and many particle problem arises from the interaction term \( U \). There are many sophisticated methods for solving the many body Schrödinger equation based on the expansion of the wave function in Slater determinants. While the simplest one is the Hartree-Fock method, more sophisticated approaches are usually categorized as post-Hartree-Fock methods. However, the problem with these methods is computational efforts, which makes it virtually impossible to apply them efficiently to larger and more complex systems.

Here DFT provides an appealing alternative, being much more versatile as it provides a way to systematically map the many body problem, with \( U \), onto a single body problem without \( U \). In DFT, the particle density \( n(\vec{r}) \) is given by,

\[
n(\vec{r}) = N \int d^3r_2 \int d^3r_3 \ldots \int d^3r_n \left( \psi^* (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) \psi (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) \right)
\]  \( \ldots (2.4) \)

Hohenberg and Kohn [16] proved in 1964 that the relation expressed above can be reversed, i.e., to a given ground state density \( n_0(\vec{r}) \), it is in principle possible to calculate the corresponding ground state wave function \( \psi_0(\vec{r}_1, \ldots, \vec{r}_n) \). In other words, \( \psi_0 \) is a unique functional of \( n_0 \), i.e.,

\[
\Psi_0 = \Psi_0[n_0]
\]  \( \ldots \ldots (2.5) \)

and consequently all other ground state observables \( O \) are also functional of \( n_0 \).

\[
\langle O \rangle[n_0] = \langle \Psi_0[n_0] | O | \Psi_0[n_0] \rangle
\]  \( \ldots \ldots (2.6) \)

From this follows, in particular, that the ground state energy is also a functional of \( n_0 \),

\[
E_o = E[n_0] = \langle \psi_o[n_0] | T + V + U | \psi_o[n_0] \rangle
\]  \( \ldots \ldots (2.7) \)

Where, the contribution of the external potential \( \langle \psi_o[n_0] | V | \psi_o[n_0] \rangle \) can be written explicitly in terms of the density.
\[ \mathcal{V}[n] = \int \mathcal{V}(\mathbf{r}) n(\mathbf{r}) d^3r \] .... (2.8)

The functionals \( T[n] \) and \( U[n] \) are called universal functional while \( V[n] \) is non-universal, as it depends on the system under study. Having specified a system \( V \), one then has to minimize the functional,

\[ E[n] = T[n] + U[n] + \int \mathcal{V}(\mathbf{r}) n(\mathbf{r}) d^3r \] .... (2.9)

A successful minimization of the energy functional will yield the ground state density \( n_0 \) and thus all other ground state observables. 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 [16]. The functional in the equation (2.8) can be written as a fictitious density functional of a non-interacting system,

\[ E_s[n] = \langle \psi_s[n] | T_s + V_s | \psi_s[n] \rangle \] .... (2.10)

Where, \( T_s \) denotes the non-interacting Kinetic energy and \( V_s \) is an external effective potential in which the particles are moving. Hence, \( n_s(\mathbf{r}) = n(\mathbf{r}) \) if \( V_s \) is chosen to be,

\[ V_s = V + U + (T - T_s) \] .... (2.11)

Thus, Kohn-Sham equations can be solved of this auxiliary non-interacting system

\[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\mathbf{r}) \Phi_i(\mathbf{r}) = E_i \Phi_i(\mathbf{r}) \] .... (2.12)

Which yields the orbitals \( \Phi_i \) that reproduce the density \( n(\mathbf{r}) \) of the original many body system,

\[ n(\mathbf{r}) = n_s(\mathbf{r}) = \sum_{i} |\Phi_i(\mathbf{r})|^2 \] .... (2.13)

The effective single-particle potential \( V_s \) can be written as

\[ V_s = V + \int \frac{e^2 n_s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3r' + V_{xc}[n_s(\mathbf{r})] \] .... (2.14)
The second term of equation (2.14) denotes the Hartree term describing the electron-electron coulomb repulsion, while the last term $V_{xc}$ is called exchange correlation potential. Here, $V_{xc}$ includes all the many-particle interactions. Since the Hartree term and $V_{xc}$ depend on $n(\vec{r})$, which depends on the $\Phi_i$, which in turn depend on $V_s$, the problem of solving the Kohn-Sham equation has to be done in a self-consistent 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 the $\Phi_i$. From these values a new density can be calculated and the whole process is started again. This procedure is then repeated until convergence is reached.

2.4.2. Applications of DFT

Kohn-Sham theory can be applied in several distinct ways depending on what is being investigated. In molecular calculations, a huge variety of exchange–correlation functionals have been developed for chemical applications. A popular functional widely used is B3LYP [9-10, 17] which is a hybrid method in which the DFT exchange functional is combined with the exact exchange functional from Hartree-Fock theory. These hybrid functionals carry adjustable parameters which are generally fitted to a training set of molecules.

2.5. Basis set

Quantum chemical calculations are typically performed within a finite set of basis functions. In these cases, the wave functions under consideration are all represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used. The operators are then represented as matrices, in this finite basis. When molecular calculations are performed, it is common to use basis composed of a finite number of atomic orbitals, centered at each atomic nucleus within the molecule. Initially, these atomic orbitals were typically Slater orbital, which corresponded to a set of functions which decayed exponentially with distance from the nuclei. These Slater-type orbitals could be approximated as linear combinations of Gaussian orbitals. It is easier to calculate overlap and other integrals with Gaussian basis functions and this led to huge computational savings of the many basis sets composed of Gaussian-type orbitals (GTOs), the smallest are called minimal basis sets and they typically composed of the minimum number of basis functions required to represent all of the electrons on each atom.
The most common addition to minimal basis sets is the addition of polarization functions, denoted by an asterisk, *. Two asterisks, **, indicate that polarization functions 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 some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen. Similarly, d-type functions can be added to a basis set with valance P orbitals, and f-functions to a basis set with d-type orbitals and so on. The precise notation indicates exactly which and how many functions are added to the basis set, such as (d,p).

Another common addition to basis sets is the addition of diffuse functions, denoted by a plus sign, +. Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These additional basis functions can be important when considering anions and other large, soft molecular system.

### 2.5.1. Minimal basis sets

A common naming convention for minimal basis set is STO-XG, where X is an integer. This X value represents the number of Gaussian primitive functions comprising a single basis function. In these basis sets, the same number of Gaussian primitives comprises core and valance orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper than their larger counter parts. The commonly used minimal basis sets are:

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

### 2.5.2. Split-valance basis sets

During most molecular bonding it is the valance electrons which principally take part in the bonding. In recognition of this fact, it is common to represent valance orbitals by more than one basis function. The notation for these split-valance basis sets is typically X-YZg. In this case, X represents the number of primitive Gaussians comprising each core atomic orbital basis function. The Y and Z indicate that the valance orbitals are composed of two basis
functions each, the first one composed of a linear combination of Y primitive Gaussian functions, the other composed of a linear combination of Z primitive Gaussian functions. In this case, the presence of two numbers after the hyphens implies that this basis set is a split – valance double –zeta basis sets are also used, denoted as X-YZWg, X-YZWVg etc. The commonly used split-valence basis sets are:

- 3-21g
- 3-21g * - polarized
- 3-21+g - Diffuse functions.
- 3-21+g* - with polarization and diffuse function
- 6-31g
- 6-31g*
- 6-31+g*
- 6-31g(3df,3pd)
- 6-311g
- 6-311g*
- 6-311+g*

2.5.3. Double, Triple, Quadruple Zeta basis sets

Basis sets in which there are multiple basis functions corresponding to each atomic orbital, including both valance orbitals and core orbitals or just the valance orbitals, are called double, triple or quadruple-zeta basis sets. Commonly used multiple Zeta basis sets are:

- CC-PVDZ-Double-zeta
- CC-PVTZ-triple-zeta
- CC-PVQZ-quadruple-zeta
- CC-PVSZ-quintuple-zeta
- aug-cc-pVDz-Augmented versions of the preceding basis sets with added diffuse functions
- TZVPP-Triple-zeta
- QZVPP-Quadruple-zeta

The ‘CC-P’ at the beginning of some of the above basis sets stands for ‘correlation consistent polarized’ basis sets. They are double/triple/quadruple/quintuple-zeta for the valance orbitals only and include successively larger shells of polarization (correlating) functions (d, f, g etc.,) that can yield convergence of the electronic energy to the complete basis set limit.
2.6. Softwares used

2.6.1. Gaussian

Gaussian 09 is a computational chemistry software program used for performing the quantum chemical calculations [12]. It is well-known that, the Gaussian program is widely-used electronic structure programs for advanced quantum chemistry research and other fields.

2.6.2. Gaussview

Gaussview is an affordable, full-featured graphical user interface for Gaussian 2009. With the help of Gaussview, one can prepare input for submission to Gaussian and to examine graphically the output that Gaussian produces. The first 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 draw a molecular structure for the calculation.

Gaussview incorporates an excellent Molecular Builder. One can use it rapidly to sketch in molecules and examine them in three dimensions. Molecules can be built by atom, ring, group, amino acid and nucleoside.

Gaussview is not integrated 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 display a variety of Gaussian calculation results, including the following:

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

Optimization of molecular geometry is a first step in quantum chemical calculation. This is mostly done on an isolated molecule in the gas phase. Geometry optimization is performed to locate the lowest energy molecular energy structure in close proximity to the specified starting structure. A geometry optimization will adjust the atomic arrangements in a molecule until an energy minimum is reached. This is the lowest position on the potential energy surface. Optimized geometry is generally used to compare with experimental data. In the absence of experimental data, construction of models is based on intuitively reasonable values for bond distances, inter-bond angles and dihedral angles.

2.8. Single point energy calculations

Single point energy gives a prediction of the energy of a molecule with specific geometry. This is usually followed by a Mulliken population analysis which is used to estimate the charge distribution. Electrostatic moments are also calculated, which then allow to calculate the dipole moments. Single point energy calculations can be performed at any level of theory, with small or large basis sets.

2.9. Potential Energy Surface scan analysis

The SCF method provides a computationally tractable means of obtaining an approximate wave function and absolute total energy for a many electron system. Many of the properties of interest can be found by constructing the full potential energy surface (PES) by performing an SCF calculation. By finding the minima on the PES, one can find stable nuclear configurations that could be observed in the laboratory and report spectroscopic information such as bond lengths, bond angles, and rotational constants to experimentalists. One can also find other stationary points on the PES which correspond to transition states for interconversion between minima and, thereby, provide experimentalists with reaction pathways and energy barriers. In order to reduce the computational effort and yet extract as much of the desired information as possible, quantum chemists use derivatives of the absolute energy [18]. From the gradient of the energy one can find stationary points such as minima and transition states by following paths of steepest ascent or descent. From the second derivative one can find the curvature of the PES around a stationary point and
predict harmonic vibrational frequencies. From higher derivatives one can find higher order spectroscopic constants such as anharmonicity [19-21].

In order to examine how one may extract such information, consider the calculation of a one–electron property such as the dipole moment. For a one–electron property the requisite operator takes the general form,

\[ \hat{\alpha} = \sum_{i} \delta_i \]

and the expectation value of \( \hat{\alpha} \) as given by Slater's rules is

\[ \langle \psi_0 | \hat{\alpha} | \psi_0 \rangle = \sum_{u,v} P_{uv} \langle \psi_u | \hat{\alpha} | \psi_v \rangle = \sum_{u,v} P_{uv} \langle v | \alpha | u \rangle \]

Where, \( P_{uv} \) is an element of the density matrix. For example, the classical definition of the dipole moment of a collection of charges \( q_i \) with position vectors \( r_i \) is given by the sum

\[ \mu = \sum_{i} q_i r_i \]

In quantum mechanics, the corresponding definition of the dipole moment of a molecule is

\[ \mu = \langle \psi_0 | \sum_{i=1}^{N} \frac{r_i}{|r_i|} | \psi_0 \rangle = \sum_{A} Z_A R_A \]

Where, the contributions of the electrons and nuclei have been separated into the first and second sums, respectively. From equation (2.18), the electronic contribution can be rewritten in terms of the known atomic orbital basis and the density matrix producing

\[ \mu = -\sum_{u,v} P_{uv} \langle v | r | u \rangle + \sum_{A} Z_A R_A \]

With the exception of the \( \langle \psi | r | \psi \rangle \) integrals which must be computed in a separate step, all of the required information is available from the SCF wave function. In conclusion, one of the most important one electron properties which can be computed in this manner is the distribution of the electrons themselves. The
charge density which represents the probability of finding an electron in a specified region of space is given by,

\[ \rho(r) = \sum_{uv} p_{uv} \phi_u(r) \phi_v^*(r) \]  

\[ \text{...... (2.20)} \]

2.10. Frequency calculations

Vibrational spectra of molecules in their ground and excited states can be computed by employing the Gaussian program. Frequency calculations are valid only at stationary points on the potential energy surface, for this reason it is necessary to run a geometry optimization prior to doing a frequency calculation. In addition to predicting the frequencies and intensities of spectra, the program can also describe the displacements of the molecule as it undergoes normal modes of vibrations. Molecular frequencies depend on the second derivative of energy with respect to the position of nuclei. Analytic second derivative are provided by the Hartree-Fock, density functional theory (B3LYP), Moller Plesset (MP2) and CASSCF theoretical procedures. An optimized energy is used as input for the frequency calculation. The frequency calculations should be performed using the same theoretical model and the basis set as the one that was used to obtain the optimized geometry of the molecule [2-26]. Harmonic force fields derived from quantum mechanics are widely used at present for the calculation of frequencies and the modes of normal vibrations [27, 28]. This opened the way to calculate the frequencies and intensities of spectral bands with a minimum degree of arbitrariness and finding the rational explanations for a number of chemical and physical properties of substances.

2.11. Scaling of force fields

SQM, the method of scaled quantum mechanical force fields [37], is a pragmatic approach to the ab initio based determination of molecular force fields. Its basis idea is to use relatively low level ab initio calculations using small basis sets and combine them with experimental information in the form 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 possible 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 usually differ appreciably from the observed
frequencies. This is partly due to the neglect of anharmonicity and partly due to approximate nature of the quantum mechanical methods. The scaling procedure fits the force field to observed (anharmonic) frequencies, therefore the scale factors correct, as far as possible, the anharmonicity. Thus, the reproduction of observed spectra may be better with SQM force fields than with the best harmonic field.

The basic features of SQM are as follows:

(1) For the reference geometry, rather than using the theoretical geometry of the quantum chemical method applied, the ideal choice would be the best experimental geometry. This eliminates a major part of the shortcomings of the HF method in predicting potential surfaces [38-40]. In practice, a reliable equilibrium structure is not always available and the theoretical geometry is corrected based on experience on small 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 [36]. 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. [38-40] introduced a formula for the scaling of a force constant $f_{ij}$:

$$f'_{ij} = \sqrt{s_i s_j} f_{ij}$$

Where the symbol $s_i$ and $s_j$ denote the scale factors for the diagonal force constants $f_{ij}$ 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.

2.12. Calculation of harmonic force fields by Molvib

Quantum mechanical methods yield harmonic force constants. On the other hand, the observed frequencies are anharmonic, but are possible to calculate the harmonic frequencies of small molecules from the observed vibrational spectra.

Normal coordinate analysis is nowadays commonly employed as an aid in the interpretation of the vibrational spectra of large molecules. In order to get meaningful results, a knowledge of vibrational force field is necessary. Since the number of force constants grows
quadratically with the number of atoms, one has to employ many approximations in the
calculation of harmonic force field even for moderately large molecules. To overcome this
difficulty, one can determine a force field for a set of related molecules using the overlay
method introduced by Snyder and Schacht Schneider in the 1960’s [31]. Gwinn developed a
program for normal coordinate analysis using mass-weighted Cartesian coordinates [32],
which eliminates the redundancy problems arising when internal valance coordinates are used
as in Wilson’s GF–method. Molvib [33-35], a FORTRAN program 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 performed in terms of mass weighted Cartesian
coordinates, instead of internal coordinates as in the conventional GF–method. This makes it
possible to overcome problems with redundant coordinates. The force field is refined by a
modified least squares fit of observed normal frequencies.

Molvib can be used for the scaling of vibrational force fields by treating the scale factors
as ordinary force constants. They can thus be calculated from a least squares fit of the calculated
and observed frequencies [35]. To perform the scale factor calculations, the program needs the
atomic coordinates, and the Cartesian force constants from an ab initio calculation. An auxiliary
program (Rdarch) is used to extract these data from the archive part of the output file of ab
initio calculations. In addition, this program can also extract the dipole derivatives and the
polarization derivatives, which are needed for intensity calculations. Molvib will convert the
Gaussian force constants, which are expressed in atomic units into the units used by the
program. Since the optimal values of the scale factors usually are less than 1, it is good to start
with an initial calculation, where all the scale factors have been set to 1, and the check that
Molvib can reproduce the frequencies calculated by the ab initio program.

In Molvib, three methods are available for the scale factor calculations. In two of these
methods, the non-diagonal terms in the potential energy will depend non–linearly on the scale
factors,

$$2\nu = \sum_i S_{ji} q_i q_j + \sum_{j\neq i} \sqrt{S_j S_i} f_{ij} q_i q_j$$

(2.37)

The factor $\sqrt{S_i S_j}$ that occurs in front of the non-diagonal force constant has to be
repeated. The frequency fit usually converges in four or five iterations, and often just a few
repetitions are necessary. The initial values for the scale factors are set to 1.
It is also possible to use individual scale factors for the non-diagonal force constants. In this case, scale factors should be associated both with diagonal and non-diagonal terms. Similar ideas have been proposed by Blom and Altona [36]. However, too many different scale factors should not be used in this case, but instead group similar factors together, so that the total number of scale factors must be very minimum. The scale factors are calculated from a least squares fit of the observed vibrations in a similar way as the force constants.

2.13. Normal coordinate analysis

Detailed description of vibrational modes can be studied by means of normal coordinate analysis. Normal coordinate analysis is a procedure for calculating the vibrational frequencies which relates the observed frequencies of preferable harmonic infrared and Raman frequencies to the force constants, equilibrium geometry and the atomic masses of the oscillating system. Normal coordinate analysis has proven useful in assigning vibrational spectra but its predictive ability depends on having reliable intramolecular force constants.

The problem of 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 determined by its kinetic and potential energies. The molecular vibrations are assumed to be simple harmonic. Analysis of molecular vibrations from classical mechanics will give valuable information for the study of molecular vibrations by quantum mechanics because of the relationship between classical and quantum mechanics.

The procedures outlined by Wilson et al [28] Nakamoto et al [29] and Colthup et al [30] have been applied in the present investigations for the treatment of normal coordinate analysis of aromatic and heterocyclic compounds.

2.13.1. Structure of molecule

Usually the structure of the molecule is available from x-ray studies or electron diffraction studies. In case the structure is not available it is assumed and the molecular parameters from the related systems are transferred.

2.13.2. Classification of normal modes

By applying Group theory, the point group symmetry of the molecule and normal modes of vibrations are classified according to the irreducible representations. Further these
vibrations are distributed to various symmetry species to which they belong. Applying IR and Raman selection rules, the number of genuine vibrations under each species is determined.

2.13.3. Internal coordinates and symmetry coordinates

Internal coordinates are the changes in bond lengths and bond angles. The symmetry coordinates are constructed from the internal coordinates and they should be normalized and orthogonalized. If \( \mathbf{R} \) is a column matrix consisting of the internal coordinates and \( \mathbf{r} \) is the column matrix of the Cartesian coordinates, then

\[
\mathbf{R} = \mathbf{B} \mathbf{r} \quad \text{...... (2.21)}
\]

Where, \( \mathbf{B} \) is the transformation matrix of the order \((3n-6)*3N\), N being the number of atoms in the molecule. If \( \mathbf{U} \) is the orthogonal transformation matrix and \( \mathbf{S} \) is a column matrix of the symmetric coordinates, then \( \mathbf{S} = \mathbf{U} \mathbf{R} \).

2.13.4. 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 selected as the internal coordinates, it implies that these coordinates are independent of each other. In complex molecules it is very difficult to recognize a redundancy in advance. If sufficient number of internal coordinates is used, the number of redundancies can be found by subtracting \(3n-6 \) (the number of internal degrees of freedom) from the number of internal coordinates. However, essential internal coordinates may have been inadvertently omitted. If a molecule has any symmetry, these considerations can be applied separately to each species. The number of independent coordinates in each species can be 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 represents redundancy. One very common form of redundancies is also likely to appear 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.
2.13.5. Potential energy matrix

The potential energy ‘V’ of a molecule is the harmonic approximation and is given by the expression,

\[ 2V = \sum_{ij} f_{ij} r_{ij} \] .......... (2.22)

Where, \( f_{ij} \) are the force constants. This equation can be written in the matrix form as,

\[ 2V = R^\prime FR \] .......... (2.23)

Which becomes in terms of symmetric co-ordinates as,

\[ 2V = S^\prime FS \] .......... (2.24)

Where,

\[ F = U^\prime F U \] .......... (2.25)

\( R^\prime, S^\prime \) and \( U^\prime \) are the transposes of \( R, S \) and \( U \) matrices respectively.

2.13.6. Kinetic energy matrix

The kinetic energy can be expressed in the form

\[ 2T = S^\prime G^{-1} S \] .......... (2.26)

Where, \( S^\prime \) is the derivative \( \frac{\partial S_i}{\partial t} \) of the \( j^{\text{th}} \) internal coordinate. \( G \) is the inverse kinetic energy matrix obtained from \( B \) matrix.

\[ G = BM^{-1}B^\prime \] .......... (2.27)

Where, \( M^{-1} \) is an inverse diagonal matrix of masses of the atoms of the molecule.

2.13.7. Secular equations

After evaluation the elements of potential and kinetic energy matrices, the secular equation.

\[ |FG - E\lambda| = 0 \] .......... (2.28)
is to be solved for evaluating the potential energy constants.

In the above equation E is the unit matrix and is a diagonal matrix and it is related to the frequencies as

$$\lambda_k = 4\pi^2 C^2 v_k^2$$  \hspace{1cm} \text{..... (2.29)}

2.13.8. Force constant refinement process

It is very difficult to solve the unsymmetrical FG matrix in the secular equation. Cyvin’s W-matrix method is followed to overcome this difficulty. The G matrix is factorized into a non-singular matrix such that

$$G = PP'$$  \hspace{1cm} \text{..... (2.30)}

Where,

P is an upper triangular matrix

P’ is a lower triangular matrix.

A trial F matrix is set up by transferring the force constants from the molecules of similar environment and by diagonalising the W Matrix.

$$W = P' F P$$  \hspace{1cm} \text{..... (2.31)}

and the values are obtained.

The process of successive approximation is continued till all the calculated frequencies are in good agreement with the observed values. This method introduces several non-vanishing off-diagonal elements in the F matrix which are useful in calculating interaction force constants.

2.13.9. Computation of L-matrix

L-matrix is obtained from the force field by factorizing the symmetrized G matrix into a product of triangular matrices T and T'.

$$G = P P'$$  \hspace{1cm} \text{..... (2.32)}

$$G = LL'$$  \hspace{1cm} \text{..... (2.33)}

But, \hspace{1cm} L = PO  \hspace{1cm} \text{..... (2.34)}
Where, $O$ is an orthogonal matrix

The secular equation $|GF - E\lambda| = 0$ can be written in the form

\[
\begin{align*}
LFL &= \Lambda \\
P'OFPO &= \Lambda \\
o'(PF)O &= \Lambda \\
o'WO &= \Lambda
\end{align*}
\]

Here, $\Lambda$ is a diagonal matrix containing Eigen values of $\lambda$ and $P'FP$ is already defined. The $O$ matrix is obtained by diagonalising the $W$ matrix so as to give the elements of matrix.

2.13.10. Potential energy distribution

In order to get the complete and accurate picture of the normal modes of vibrations, the potential energy distribution (PED) has to be calculated in the present investigation using the relation,

\[
PED = \frac{F_{ii}L_{ia}^2}{\lambda_a^2}
\]

Where,

$F_{ii}$ is the potential energy constant,
$L_{ia}$ is the $L$ matrix element and
$\lambda_a$ is equal to $4\pi^2c^2V_a^2$.

2.14. Solvation models

One can carry out accurate gas-phase calculations and then make broad generalization about how the surrounding condensed phase may influence the results. The condensed-phase effects are small for the properties being studied, but it is useful in a qualitative sense. To determine nature of the medium one must consider solvation process. Different physical effects contribute to the overall solvation process and the most important components of solvation process are electrostatic interactions, cavitation, change in dispersion and changes in bulk solvent structure. Several solvation models are available in quantum mechanical procedures each having definite merits. The integral equation formalism (IEF) solvation method involves solutes in a liquid phase, using the permittivity for characterization of the solvent. IEF solvation
model is a member of the PCM group implemented in Gaussian version 09, and it has become the default PCM formulation [41-44]. In IEF, the potentials are redefined in terms of the proper Greens functions \( G(x, y) \) and is the potential produced in \( x \) by a unit point charge located in \( y \). However, in several cases the Green function can be effectively built numerically, and thus the IEF approach can be generalized to many other environments as, for example, a diffuse interface with an electric permittivity depending on the position. Various spectroscopic techniques were employed for the present work, the instrumentation of FT-IR, FT-Raman and UV-Visible are discussed in the next chapter.

2.15. Theory of Frontier Molecular Orbitals

Woodward and Hoffmann first introduced the idea of so-called “frontier orbitals” (the HOMO and LUMO) often provide the key to understand why some chemical reactions proceed easily whereas others do not. Electronic interactions are represented by the molecular orbitals, which also involve \( \sigma \)-orbitals (sp\(^2\) hybridized for alkenes) (1) and \( \pi \)-orbitals (2). In a typical alkene, bonding is described in terms of the \( \sigma \)- and \( \pi \)-orbitals. Highest occupied molecular
orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor [45]. The MOs are defined as Eigen functions of the Fock operator, which exhibits the full symmetry of the nuclear point group, they necessarily form a basis for irreducible representations of full point–group symmetry. These molecular orbitals take on a directional character [represented by (+ or dark) and (− or light)] when they are in close proximity to another atom, orbital, or polarized species, as is the case in a covalent bond. There are, therefore, two possibilities when two sp\(^2\) hybridized orbitals come together. Orbitals of the same sign can be directed toward each other, as in 3, or orbitals of opposite sign can be directed toward each other, as in 4. In 3, the electron density between the two nuclei is maximized (electronic attraction for the positive nucleus) but in 4 it is minimized. Since a strong covalent bond (mutual sharing of electron density between nuclei) is associated with significant electron density between the nuclei, 3 represents a bonding interaction and 4 can be viewed as an antibonding interaction. These terms have meaning only when we consider the valence orbitals.

Similar arguments can be made for the overlap of p-orbitals that constitutes a \(\pi\) bond. In 5, the overlap of orbitals with the same sign represents the maximum bonding interaction for the \(\pi\)-bond of ethylene, and 6 represents an antibonding molecular orbital. Figure 2.2 shows the net energy of the bonding interaction in a \(\pi\) bond with that of \(\sigma\)-bond is lower than that of the antibonding interaction and is more stable. The energy of each molecular orbital along with their energy difference (\(\Delta E\)) can be measured. It was found that this varies with substituents on the alkene, which has important implications for the reactivity of these compounds as shown in Figure 2.2.

The difference in energy between the two \(\pi\) molecular orbitals (5 and 6) can be represented in terms of their relative energies as shown in Figure 2.2 taken from Hoz's work [47]. In terms of chemical reactivity, HOMO is the orbital that donate electrons. Energy of HOMO is the negative of ionization potential (IP), which is a reasonable measure of its energy [46,47]. The higher energy orbital does not contain electrons, but is the next available energy level if electrons are present. Figure 2.3 shows various bonding and antibonding combinations and their representations. Electron affinity (EA) is the energy that describes electron accepting capability and this orbital is called the lowest unoccupied molecular orbital, the LUMO. The energy of the LUMO is taken to be the negative of the EA of the alkene [46,47]. In a simplest
way, the LUMO would be expected to accept electrons from the HOMO of another \( \pi \) bond. From the pioneering work of Fukui, the reactive HOMO and LUMO of any molecule are referred to as frontier molecular orbitals (FMO). The energy difference between the HOMO and LUMO is termed the HOMO-LUMO gap and it is shown in Figure 2.4.

**Figure 2.3. Various bonding and antibonding combinations**
Figure 2.4. HOMO–LUMO energy gap

Fukui realized that a good reactivity approximation could be obtained by looking at the frontier orbitals and this is possible based on three main observations of molecular orbital theory as two molecules interact:

1. The occupied orbitals of different molecules repel each other.

2. Positive charges of one molecule attract the negative charges of the other.

3. The occupied orbitals of one molecule and the unoccupied orbitals of the other (especially the HOMO and LUMO) interact with each other causing attraction.

2.16. Theory of Natural bond orbital analysis

Natural bond orbital (NBO) analysis originated as a technique for studying hybridization and covalency effects in polyatomic wave functions, based on local block eigenvectors of the one-particle density matrix [48]. NBOs were considered to be a chemist’s basis set which reflects the picture of localized bonds and lone pairs as basic units of molecular structure. The Natural Localized Molecular orbitals (NLMOs) are formed from Natural Bond Orbitals (NBOs), which in turn was formed from the Natural Hybrid Orbitals (NHOs) and these NHOs are formed from Natural Atomic Orbitals (NAOs).
NBO analysis also differs from earlier methods of wave function analysis that employ alternative criteria to define filled and unfilled orbitals or that allow overlap of these orbitals. In general, NBO analysis allows one to isolate H-bond interaction energies in low-order perturbative expressions of easily interpreted form and to relate these expressions to chemical explanations of H-bonding based on orbital interaction concepts. The results from NBO analysis are often surprisingly in close agreement with qualitative concepts that preceded the era of large-scale computations. This analysis has thus tended to differ from other analysis methods in suggesting how modern ab initio wave functions can be brought into essential harmony with earlier qualitative viewpoints [49-52].

NBO analysis comprises a sequence of transformations from the input basis set to various localized basis sets [natural atomic orbitals (NAOs), hybrid orbitals (NHOs), bond orbitals (NBOs), and localized molecular orbitals (NLMOs)].

\[
\text{Input basis} \rightarrow \text{NAOs} \rightarrow \text{NHOs} \rightarrow \text{NBOs} \rightarrow \text{NLMOs} \quad \cdots \quad (2.39)
\]

These localized sets may subsequently be transformed to delocalized natural orbitals (NOS) or canonical molecular orbitals (MOs). The NBO computer programs which has been attached to a variety of ab initio and semi-empirical electronic etc., automates the above said steps. The exact representation of the calculated wave function and operators (properties) of the system was given involving the use of each step of the sequence (2.39).

2.16.1. Hyperconjugative interactions in NBO analysis

The hyperconjugative $\sigma \rightarrow \sigma^*$ interactions play a highly important role in NBO analysis. These interactions represent the weak departures from a strictly localized natural Lewis structure that constitute the primary “non-covalent” effects. The $\sigma \rightarrow \sigma^*$ interactions are manifested in a variety of forms in NBO analysis:

(i) Direct variational energy lowering (and corresponding geometry changes) associated with the deletion of specific $\sigma^*$ basis orbitals or specific $P_{\sigma^*}$ matrix elements
(ii) Changes in second-order energies associated with the $P_{\sigma^*}$ interaction
(iii) Changes in the natural populations $q_\sigma$ and $q_{\sigma^*}$ of the hyper conjugating orbitals
(iv) Changes in the overlap integral $(\sigma|\sigma^*)$ of associated pre-NBOs $\sigma$ and $\sigma^*$ and
(v) Changes in the delocalization tails of LMOs.
However, it was natural to observe that the unfilled valence $\sigma^*$ orbitals might also play an important role in intermolecular interactions. The intermolecular $\sigma \rightarrow \sigma^*$ interactions could be expected to be particularly important. Among covalently bonded molecules, this requirement is uniquely satisfied by $\sigma_{\text{AH}}^*$ hydride antibonds, particularly when a strong polarization of $\sigma_{\text{AH}}^*$ toward the outer end of the orbital takes place due to the electronegativity of A. The best donor orbital for such an interaction would be expected to be a diffuse lone pair $n_D$.

Hyperconjugation refers to the interaction of orbital of a single bond with the $\pi$-orbital of an adjacent double/triple bond. In C-H bonds, the hyperconjugation causes the releasing of electronic charge from a $\pi_{\text{CH}}$ to the C-C bond [53]. As a result, C-C bond length decreases and the bond strength increases. Due to the release of electronic charge from $\pi_{\text{CH}}$, the increase of charge on hydrogen occurs which results in more acidic nature. This will increase the C-H bond ionicity and decreases the C-H bond strength. In other case, the decrease of electronic charge in $\pi_{\text{CH}}$ bonding orbital, there should be decrease in strength of C-H. Owing to suitable balance between these two opposing effects, the bond length and spectral characteristics of C-H bonds of the hyperconjugated systems do not show direct correlation with the charge on hydrogen.

### 2.16.2. Intramolecular charge transfer (ICT)

The compounds having the electron donor and electron acceptor at the end positions of the $\pi$-conjugated system is related to the existence of large intramolecular charge transfer. The ICT causes the electron releasing effect in the acceptor moiety, affecting the spectral modes. C=C stretching mode of acceptor subunit occurs at lower wavenumber compared to the corresponding mode of the donor subunit [54-56]. Along the conjugated path, ICT induces large variation in the molecular polarizability as well as in the dipole moment simultaneously during vibration. This produces the IR and Raman intensity for the same mode thus arising the comparable intensities of IR and Raman bands from the vibrations of conjugated system. The electron donating effect of donor unit also causes wavenumber shifting in the vibrations of the donor group. The existence of a large ICT at relatively low energy values depends on the efficiency of the $\pi$-electron delocalization through the bridge and of the electron donor and the electron-acceptor strength of the end groups.
2.16.3. Relationship between Intermolecular and Intramolecular Interactions

One of the main applications of bond orbital analysis was to study the internal rotation barrier of molecules. It was found that the rotation barrier practically disappears or gets reversed in sign upon removal of the $\sigma^*_{CH}$ orbitals from the basis set. The rotation barrier can thus be attributed to $\sigma\rightarrow\sigma^*$ hyperconjugation. The $\sigma\rightarrow\sigma^*$ interaction was found to be increased when the accepting antibond was made more polar and decreased when the donor bond was made more polar. Replacement of the $\sigma$ donor with a lone pair donor $n$ significantly increases the interaction with the $\sigma^*$ orbital. Such $n\rightarrow\sigma^*$ interactions constitute negative hyperconjugation.

Coupling between intermolecular and intramolecular donor-acceptor interactions is of enormous biological importance. The interactions between functional groups on enzymes and substrates at active sites induce intramolecular changes that enhance the direct substrate reactivity. The intramolecular vibrational excitation directly affects the strength of both intra- and intermolecular forces. An interest has been built in the case of vibrationally excited A-H bonds, since hybrid bonds exhibit the large anharmonicities which make it feasible by laser overtone spectroscopy to excite high-$u$ states selectively. It is recognized from the donor-acceptor picture that elongation of A-H bond through vibrational excitation should generally increase the acceptor strength of the associated $\sigma^*$ hydride antibond, making it a better Lewis acid.
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