2.1 INTRODUCTION

Quantum mechanics is the basis for the computational chemistry calculations. Computational chemistry involves the application of mathematical and the theoretical principles to the solution of chemical problems. Furthermore, it is used as a tool by researchers to investigate molecular structure, properties, kinetics and reactivity. Advanced computer programs are used for performing quantum chemical calculations on a wide range of molecules. There are two broad areas within computational chemistry: molecular mechanics and electronic structure theory.

2.2 MOLECULAR MECHANICS

Molecular Mechanics (MM) is based on a mathematical model of a molecule as a collection of balls (corresponding to the atoms) held together by springs (corresponding to the bonds). The principle behind MM is to express the energy of a molecule as a function of its resistance towards bond stretching, bond bending and atom crowding, and to use this energy equation to find the bond lengths, angles and dihedrals corresponding to the minimum energy geometry, to the various possible potential energy surface minima. MM uses a conceptually mechanical model of a molecule to find its minimum energy geometry. The form of the mathematical expression for the energy, and the parameters constitute a force field, and the MM methods are called force field methods. The negative of the first derivative of the potential energy of the particle with respect to displacement along some direction is the force on the particle. A “force field” E can be differentiated to give the force on each atom.

2.3 ELECTRONIC STRUCTURE METHODS

The electronic structure of molecules is determined by the equations of quantum mechanics. Quantum mechanics states that the energy and other related...
properties (structure, bonding, spectroscopy, reactivity) of the molecule can be obtained by solving the Schrödinger equation

\[ H\psi = E\psi \]

The electronic structure methods are characterized by various mathematical approximations and solutions. There are two major classes of electronic structure methods. The semi-empirical method plugging of experimental values into a mathematical procedure to get the best calculated values is called parameterization. It is the mixing of theory and experiment that makes the method “Semi-empirical”. It is based on the Schrödinger equation, but parameterized with experiment.

Ab-initio methods are based on the Schrödinger equation. The ab-initio method solves the Schrödinger equation for a molecule and gives the energy and wave function of the molecules. The wave function is a mathematical function that can be used to calculate the electron distribution.

2.3.1 Uses of Ab-initio methods

The main uses of the ab-initio method are calculating molecular geometries, energies, vibrational frequencies, spectra (IR, Raman and UV), ionization potentials, electron affinities, and properties like dipole moments which are directly connected with electron distribution. The visualization of calculated phenomena, such as molecular vibrations, charge distributions and molecular orbitals, can be very important in interpreting the results of calculations [1].

2.4 DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) is a quantum mechanical modeling method used 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 popular and versatile methods available in condensed matter physics and
computation chemistry. Traditional 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 density as the basic quantity. Whereas the many body wave functions are 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 the density functional theory has its conceptual roots in the Thomas Fermi model, the DFT was put on a firm theoretical footing by Hohenberg and Kohn theorems. 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 problems 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, e.g. the exchange and correlation interactions [2].

**2.4.1 Density Functional Theory using Hohenberg and Kohn Theorem**

Density functional theory (DFT) is a quantum mechanical method used for the calculation of electronic structure and properties of many body systems [3]. Hohenberg and Kohn [4] proved that the ground state energy and all other electronic properties of an atom or a molecule are uniquely determined by the ground state
density. Since $\rho$ is a function of the electronic coordinates, and energy is a function of $\rho$, $E[\rho]$. The ground state energy functional can be written as

$$E[\rho] = T_{ni}[\rho] + V_{en}[\rho] + V_{ee}[\rho] + \Delta T[\rho] + \Delta V_{ee}[\rho]$$  \hspace{1cm} (2.1)

Where $T_{ni}$ is the kinetic energy of the non-interacting electrons, $V_{en}$ is the electron-nucleus attraction energy and $V_{ee}$ is the Coulomb repulsion energy of the electrons, $\Delta T$ is the correction to the kinetic energy due to the interacting nature of the electrons and $\Delta V_{ee}$ is the correction to the electronic repulsion energy. The last two terms are combined together in a single term and the above equation is written as

$$E[\rho] = T_{ni}[\rho] + V_{en}[\rho] + V_{ee}[\rho] + E_{xc}[\rho]$$  \hspace{1cm} (2.2)

where $E_{xc}[\rho]$ is called the exchange correlation energy functional. The exact ground energy of a molecule with $N$ electrons and $N'$ nuclei can be written as

$$E[\rho]=\frac{1}{2} \sum_{i=1}^{N} \int \nabla \Psi_i^*(r_1) \nabla \Psi_i(r_1) dr_1 - \sum_{A=1}^{N'} \frac{Z_A}{r_{A1}} \rho(r_1) dr_1 + \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} dr_1 dr_2 + E_{xc}[\rho]$$  \hspace{1cm} (2.3)

where $\Psi_i$'s are one-electron functions called the Kohn-Shan (KS) orbitals. The exact ground state density is given by

$$\rho(r) = \sum_{i=1}^{N} |\Psi_i(r)|^2$$  \hspace{1cm} (2.4)

Obviously, $\int \rho(r) dr = N$. This expression of $\rho(r)$ and those for the first three atoms in equation (2.3) correspond to Slater determinantal wavefunction ($\psi_S$) constructed from the KS orbitals. The energy expectation value of $\psi_S$ is given by

$$E_{KS} = <\psi_S|H|\psi_S>$$

$$= -\frac{1}{2} \sum_{i=1}^{N} \int \nabla \Psi_i^*(r_1) \nabla \Psi_i(r_1) dr_1 - \sum_{A=1}^{N'} \frac{Z_A}{r_{A1}} \rho(r_1) dr_1 + \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} dr_1 dr_2$$

$$- \frac{1}{2} \int \sum_i \sum_j \int \frac{\Psi_i^*(r_1) \Psi_j^*(r_2) \Psi_i(r_1) \Psi_j(r_2)}{r_{12}} dr_1 dr_2$$  \hspace{1cm} (2.5)
The KS orbitals are the solutions of the equation,

\[ F_{KS}(r_1)\Psi_i(r_1) = \varepsilon_i \Psi_i(r_1) \quad \cdots (2.6) \]

where \( \varepsilon_i \) is the orbital energy and

\[
F_{KS} = \frac{-\nabla_i^2}{2} - \sum_{\alpha=1}^{N} \frac{z_{\alpha}}{r_{1\alpha}} + \int \frac{p(r_2)}{r_{12}} \, dr_2 + V_{xc}(r_1) \quad \cdots (2.7)
\]

The last term in the RHS is called the exchange correlation potential. It is defined as the functional derivative of \( E_{xc}[\rho] \), i.e.,

\[
V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad \cdots (2.8)
\]

Since the exact form of this functional cannot be defined, several approximate schemes have been developed. Of these, the simplest one is the local density approximation (LDA). In this approximation,

\[
E_{xc}^{LDA}[\rho] = \int \varepsilon_{xc}[\rho(r)] \, dr \quad \cdots (2.9)
\]

where \( \varepsilon_{xc} \) is the exchange correlation energy per electron in a homogeneous electron gas of constant density. A homogeneous electron gas is a hypothetical electroneutral system consisting of an infinite number of electrons moving in a space of infinite volume in which positive charge is continuously and uniformly distributed. The LDA is not strictly valid in molecules where the positive charge, instead of being uniformly distributed, is localized at the nuclear positions. This implies that \( \rho(r) \) cannot be uniform. Thus \( E_{xc}[\rho] \) is made to depend not only on the local value of the density, but also on the manner in which the density is locally changing, i.e., on the gradient of the density. This is called the generalized gradient approximation (GGA).

The GGA nonlocal functional is defined as

\[
E_{xc}^{GGA}[\rho] = \int f(\rho, |\rho'(r)|) \, dr \quad \cdots (2.10)
\]

Where \( \rho'(r) = \nabla \rho(r) \).
The GGA exchange ($E_x$) and correlation ($E_c$) functionals are generally determined separately. Quite often, instead of using a pure DFT functional, a combination of $E_x^{HF}$, $E_x^{DFT}$ and $E_c^{DFT}$ is used. The resulting functional is called a hybrid functional. Of the several such functionals that have been proposed, the one designated by the acronym B3LYP is most widely used. B3LYP stands for the nonlocal three-parameter exchange functional of Becke and the nonlocal correlation functional of Lee, Yang and Parr.

Once the functional form of $E_{xc}$ is chosen, equation (2.6) can be solved iteratively in a self-consistent manner. From an initial guess of $\rho(r)$, one determines $E_{xc}[\rho]$ using which $V_{xc}[\rho]$ can be calculated. Inserting $V_{xc}[\rho]$ thus obtained in equation (2.7) and solving equation (2.6) one gets an initial set of KS orbitals. These are used in equation (2.4) to obtain improved $\rho(r)$. The sequence $\rho(r) \rightarrow E_{xc}[\rho] \rightarrow V_{xc}[\rho] \rightarrow \Psi_i(r) \rightarrow \rho(r)$ is repeated until the density and the exchange correlation energy have converged to a given tolerance limit.

### 2.5 BASIS SET

A basis set is a mathematical description of the orbitals within a system used to perform the theoretical calculation. The basis set can be interpreted as restricting each electron to a particular region of space. Larger basis sets impose fewer constrains on electrons and approximate each orbital more accurately but require more computational resources. Standard basis sets for electronic structure calculations use linear combinations of basis functions (one- electron functions) to form the orbitals.

Gaussian and other ab-initio electronic structure programs use basis functions which are themselves composed of a linear combination of Gaussian functions; such basis functions are referred to as contracted functions, and the
component Gaussian functions are referred as primitives. A basis function consisting of a single Gaussian function is termed uncontract [5].

In modern quantum chemical calculations are typically performed within a finite set of basis functions. Gaussian 03W and other ab-initio electronic structure programs use Gaussian type atomic functions as basis functions. A basis set is the mathematical description of the orbitals within a system (which in turn combine to approximate the total electronic wave functions) used to perform theoretical calculation. 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 preformed, it is common to use basis composed of a finite number of atomic orbitals, centered at each atomic nucleus within the molecule. Initially, 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 (STO) 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 basis sets composed of Gaussian-type orbitals (GTOs), the smallest are called minimal basis sets and they are 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 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 and soft molecular system.

Basis sets may be classified as minimal basis sets and split-valence basis sets. The STO-3G basis set is an example of the minimal basis set, while the 3-21G, 6-31G and 6-311G basis sets are examples of the split-valence basis set. Minimal basis sets make use of only those functions needed to accommodate all of the electrons of the atom maintaining a spherical geometry. These functions are the 1s function (for H and He) and a set of five functions: 1s, 2s, 2pₓ, 2pᵧ and 2p₂ for Li to Ne. As a consequence, those molecules that have atoms with spherical environments will be better represented than those that have non-spherical environments. The split valence basis sets incorporate sets of valence basis functions, whereby the resulting orbitals can better represent anisotropic electron distribution in molecules in terms of both σ and π bonds. This is achieved by including two sets of valence basis functions that will account for orbitals involved in σ and π bonding in terms of linear combinations of the said functions. In these basis sets, atoms are represented by one set of functions that accounts for the inner-shell electrons, and two sets of functions that account for bonding electrons. Split valence basis sets may be a minimal split-valence basis set (like the 3-21G*), or a fully flexible split valence basis set (like the 6-31G*). Displacement of electron distribution away from the
nuclei can be achieved by providing p-type functions on H, and d-type functions for heavier atoms. These sets are termed polarization basis sets and the d-type functions, are known as polarization functions. Polarization basis sets such as 6-31G*, 6-31G** and 6-311G* are constituted by a set of functions that represents the core electrons, two or more sets of functions that represent valence electrons and a set of d-type polarization functions that account for electronic distribution between nuclei. The polarization functions adjust the orbital shape by adding an orbital angular momentum one quantum level higher than the valence orbitals. An * add sd function to heavy atoms, while ** add sp function to H, in addition to adding d function to heavy atoms. Other possible basis sets, like 6-31+G* and 6-311+G**, incorporate diffuse functions, which are employed for electrons with large radial extent, and hence are useful in describing anions, molecules with lone pairs, excited states and transition states, and in absolute acidity calculations.

The Gaussian primitives have the same angular momentum as valence orbitals but have much small exponents, so allowing for some electron density at large distances from the nuclei. In these basis sets, normally only the heavy atoms (and occasionally hydrogen) are provided with diffuse functions. A + adds larger p function to heavy atoms, while ++ add sp and s type function to the heavy atom and to H, respectively.

2.6 POTENTIAL ENERGY SURFACE STUDY (PES)

A PES is the relationship between the energy of a molecule and its geometry. This relaxed potential energy surface scan can be performed automatically in either a Z-matrix or redundant internal coordinate system. The potential minima found were optimized at the B3LYP/6-311++G (d, p) level of theory. During all the scans one set of dihedrals was kept frozen to reduce the dimensionality of our study. However, all
torsional angles were allowed to relax during optimization of potential minima derived from earlier scans.

The positions of the energy minima along the reaction coordinate give the equilibrium structures of the reactants and products. The position of the energy maximum defines the transition state. Reactants, products and transition states are all stationary points on the potential energy diagram. In the many-dimensional case, all partial derivatives of the energy with respect to each of the $3N-6$ ($N$ atoms) independent geometrical coordinates ($R_i$) are zero:

$$\frac{dV}{dR_i} = 0, \quad i=1,2,3,\ldots,3N-6$$

The reactants and products are energy minima and are characterized by a positive second energy derivative. The transition state is an energy maximum and is characterized by a negative second energy derivative [6].

**2.7 NATURAL BOND ORBITAL (NBO) ANALYSIS**

The Natural bond orbital (NBO) analysis [7] was originated as a technique for studying hybridization and covalence effects in polyatomic wave functions. The work of Foster and Weinhold was extended by Reed et al. who employed NBO analysis that exhibited particularly H-bonded and other strongly bound van der Waals complexes [8]. The ab-initio wave functions transformed to NBO form are found to be in good agreement with the Lewis structure concepts and with the basic Pauling-Slater-Coulson picture [9, 10] of bond hybridization and polarization. The filled NBOs of the “natural Lewis structure” are well adapted to describing covalence effects in molecules [8]. However, the general transformation to NBOs also leads to orbitals that are unoccupied in the formal Lewis structure and that may be used to describe non-covalent effects. The symbols $\sigma$ and $\sigma^*$ are used in a generic sense to refer to filled and unfilled orbitals of the formal Lewis structure, though the formal
orbital may actually be core orbitals (C), lone pair (n), σ or π bonds (σ, π) and so forth, the latter may be σ or π antibonds (σ*, π*), extra valence shell Rydberg (r) orbitals and so forth, according to the specific case.

The antibonds represent the unused valence-shell capacity and the spanning portions of the valence space that are formally unsaturated by covalent bond formation. The non-covalent delocalization effects are associated with σ→σ* interactions between filled (donor) and unfilled (acceptor) orbitals, and it is natural to describe them as being of “donor-acceptor”, charge transfer, or generalized “Lewis base-Lewis acid” type. The NBO calculations [11] were performed using NBO 3.1 program [12] as implemented in the Gaussian 03W package [13] at the HF and DFT methods with basis sets.

2.7.1 Second-Order Perturbation Theory Analysis

The second-order perturbation 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 [14]. The interactions result 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) associated with delocalization ("2e-stabilization") i→j is estimated as

\[ E(2) = \Delta E_{ij} = q_i \frac{F_{ij}^2}{(\varepsilon_j - \varepsilon_i)} \] ... (2.11)

where \( q_i \) is the donor orbital occupancy, \( \varepsilon_i, \varepsilon_j \) are diagonal elements (orbital energies) and \( F_{ij} \) is the off-diagonal NBO Fock matrix element.

The localized orbitals in the Lewis structure can interact strongly. A filled bonding or lone pair orbital can act as a donor and an empty or filled bonding, antibonding, or lone pair orbital can act as an acceptor. These interactions can
strengthen and weaken bonds. For example, a lone pair donor→antibonding acceptor orbital interaction may weaken the bond associated with the antibonding orbital. Conversely, an interaction with a bonding pair as the acceptor will strengthen the bond. Strong electron delocalization in best Lewis structure will also show up as donor-acceptor interactions.

2.8 FRONTIER MOLECULAR ORBITALS

The most important frontier molecular orbitals (FMOs) such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plays a crucial part in the chemical stability of the molecule [15]. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that accepts electrons. The HOMO represents the ability to donate an electron and LUMO as an electron acceptor represents the ability to accept an electron. The energy gap between HOMO and LUMO also determines the chemical reactivity, optical polarizability and chemical hardness and softness of the molecule [16].

2.9 MOLECULAR ELECTROSTATIC POTENTIAL (MESP)

Electrostatic potential maps, also known as molecular electrical potential surfaces illustrate the charge distributions of molecules three dimensionally. These maps allow visualizing variably charged regions of a molecule. Knowledge of the charge distributions can be used to determine how molecules interact with one another. Electrostatic potential energy maps also allow visualizing the size and shape of molecules. In organic chemistry, electrostatic potential maps are invaluable in predicting the behavior of complex molecules.
To analyze the charge distribution of a molecule accurately, a very large quantity of electrostatic potential energy values must be calculated. The best way to convey this data is to visually represent it, as in an electrostatic potential map. A computer program then imposes the calculated data onto an electron density model of the molecule derived from the Schrodinger equation. To make the electrostatic potential energy data easy to interpret, a colour spectrum with red as the lowest electrostatic potential energy value and blue as the highest is employed to convey the varying intensities of the electrostatic potential energy values [17].

**2.10 SCALING OF FORCE_FIELDS**

SQM, the method of scaled quantum mechanical force fields [18] 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. The 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 the 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 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 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 [19]. In practice, a reliable equilibrium structure is not always available and 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 [20]. 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. [18] introduced a formula for the scaling of force constants $f_{ij}$:

$$f'_{ij} = \sqrt{S_i S_j f_{ij}}$$

where the symbol $S_i$ and $S_j$ denote the scale factors for the diagonal force constants $f_{ii}$ 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.

2.10.1 Scaling of Ab-Initio Force fields by MOLVIB

The 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. 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 the approximate nature of the quantum mechanical methods.

Normal coordinate analysis is now-a-days commonly 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 necessary. Since the number of force constants grows quadratically with the number of atoms, many approximations in the calculation of harmonic force field had been employed 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 Schachtschneider in the 1960’s [21]. Gwinn developed a program for normal coordinate analysis using mass-weighted Cartesian coordinates [22], which eliminates the redundancy problems arising when internal valance coordinates are used as in Wilson’s GF-method. MOLVIB [23, 24], a FORTRAN program is based on the above idea developed for the calculation of harmonic force fields and vibrational modes of molecules with up to 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 [25]. 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 out 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 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 as,

\[
2V = \sum_i S_i f_{ij} q_i q_j + \sum_{i \neq j} \sqrt{S_i S_j} f_{ij} q_i q_j \quad \text{(2.11)}
\]

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 [20]. 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 square fit of the observed vibrations in a
similar way as the force constants.

**2.11 NORMAL COORDINATE ANALYSIS**

Normal coordinate analysis is a procedure for calculating the vibrational
frequencies which relate the observed frequencies (infrared and Raman frequencies)
to the force constants, equilibrium geometry and the atomic masses of the oscillating
system. The normal coordinate analysis is very useful and necessary for the complete assignment of the vibrational frequencies of a polyatomic molecule and for a quantitative description of the vibrations. The intramolecular force constants are related to the electronic structure and are correlated with bond nature, electron delocalization and interatomic repulsions. It is also useful, in the quantitative study of vibrational band intensities and to study the interaction between vibration and rotation levels.

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 [26].

2.12 ELECTRONIC SPECTRA

Electronic spectra are the basis for many chemical-physical molecular features. Computations can easily analyze the different chemical-physical effects by modulating the spectral properties of the molecule. Many interesting chemical problems involve in both the ground and exited states of molecules. Density functional theory (DFT) has provided a successful description, only for the ground state properties of atoms, molecules and solids. Therefore, the DFT formalism has to be extended to excited states in order to describe the photochemical and photophysical processes. Time-dependent DFT (TD-DFT) has become an effective tool for excited state calculations [27].
The calculation of multiple energies requires the energies of excited determinants, such as occupied spin-orbital number $i$ to the empty spin-orbital number $j$, to be computed. Thus certain states are referred to as $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions. The time-dependent generalization of the DFT formalism offers a rigorous route to the calculation of the dynamic response of charge density. This allows the determination of the electronic excitation spectrum in the usual dipole approximation, since the poles of the dynamic polarizability determine the excitation energies [28]. The strengths of the poles are given by the oscillator strengths $f$, or equivalently by the transition dipole moment $\mu$, i.e. the intensity of the optical transitions.
REFERENCES


