CHAPTER - II
QUANTUM CHEMICAL CALCULATIONS AND NORMAL COORDINATE ANALYSIS

2.1. INTRODUCTION

The assignment of vibrational spectra of polyatomic molecule is essential for the study of molecular geometries and force constants. Despite the significant advances in the instrumentation aspects of spectrophotometers, still difficulties may arise due to the overlapping of bands, band contours etc. Now-a-days, with the development of sophisticated computational methods of theoretical chemistry, the vibrational frequencies and their intensities can be predicted theoretically and the vibrational spectra can also be simulated by applying quantum chemical methods.

Molecular mechanics deals with the changes in the electronic energy of the molecule due to bond stretching \( V_b \), bond angle bending \( V_\theta \), out-of-plane bending \( V_{0\theta} \), internal rotation (torsion) about bonds \( V_\phi \), interactions between different kinds of motions \( V_{\text{int}} \), Van der Waals attractions and repulsions between non-bonded atoms \( V_{\text{vdw}} \) and electrostatic interactions between atoms \( V_{\text{es}} \). The sum of these contributions gives the potential energy in the molecular mechanics frame work \( V \) for the motion of the atoms in the molecule. It is often called 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:

\[
V(X^N) = \sum_{i=1}^{k} V_i \quad \ldots \quad (2.1)
\]
where \( V \) represents the potential energy of the molecular system, which is a function of the Cartesian coordinates of all atoms denoted as \( X^{\text{H}}S \). The equation (2.1) can be written as

\[
V = V_b + V_q + V_r + V_{\text{q-r}} + V_{\text{es}} + V_{\text{vdw}} + V_{\text{int}} 
\]  
… (2.2)

### 2.1.1. Energy Minimizations

The potential energy calculated by summing up the energies of various interactions is a numerical value for a single conformation. Energy minimization is usually performed by gradient optimization, atoms are moved so as to reduce the net force on them. The minimized structure has small forces on each atom and therefore serves as an excellent starting point for molecular dynamics simulation.

A molecular mechanics geometry optimization starts with the initially assumed geometry and finds the nearest local energy minimum by minimizing the steric energy \( V \) of the equation (2.2). This equation provides an analytical form for the energy, the first and second derivatives of \( V \) can easily be evaluated analytically, facilitates which energy minimization. Many programs of molecular mechanics have built in searching methods that locate many low-energy conformers. Force field methods are primarily geared to predict two properties, geometries and relative energies.

### 2.2. **Ab Initio** Methods

*Ab initio* orbital molecular methods are useful to predict harmonic force constants and frequencies of normal modes. The *ab initio* methods first optimize the molecular geometry and then evaluate the second derivative at the equilibrium positions usually using analytical derivatives. Such methods provide reliable values
for harmonic vibrational 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 gives 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 force constants in internal or symmetry coordinates. Ab initio calculations followed by normal coordinate analysis are very helpful in making reliable vibrational assignments. Band intensities from ab initio studies are another important output. Such band intensity data can also be very useful in making vibrational assignments. Two principally different quantum mechanical methods addressing the vibrational problems are namely Hartree-Fock method and Density Functional Theories (DFT). Density functional theory calculation has emerged in the past few years as successful alternative to traditional Hartree-Fock method. The DFT methods, particularly hybrid functional methods [57-60] have evolved a powerful quantum chemical tool for the determination of the electronic structure of molecules. In the frame work of DFT approach, different exchange and correlation functionals are routinely used. Among these, the Becke-3-Lee-Yang-Parr (B3LYP) combination [61,62] is the mostly used since it proved its ability in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and standard various basis sets, provide an excellent compromise between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The vibrational
frequencies calculated by applying DFT methods are normally overestimated than experimental values by 2-5% on an average. This overestimation is due to the neglect of electron correlation, anharmonicities, and incomplete basis sets.

This overestimation can be narrowed down by empirical scaling factors ranging from 0.8 to 1.0. The scaling factors depend both on method and basis sets and they are partially compensated for the systemic errors in the calculation of frequencies. Selective scaling, multiple scaling are some scaling methods advocated to minimize the overestimation of the frequency differences. *Ab initio* calculation could be performed using GAUSSIAN 09 software package [63].

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 leads to errors in the assignment of the experimental frequencies. Therefore, determining empirical corrections to quantum mechanical force fields is important. It is shown that [64-66] of all the methods for empirically correcting quantum-mechanical force fields, the one with the best physical basis are the modern version of the Pulay method.

A simple flow chart which explains the complete scheme of calculation by quantum chemical methods is shown in Fig. 2.1.

### 2.3. 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.
Fig. 2.1: Flow diagram of program used in the quantum chemical calculations
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. 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 minimises 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. 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 has 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 are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom.

When polarization is added to the basis set, a p-function is added to that 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.
2.4.1. 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 counterparts. The commonly used minimal basis sets are:

- STO-2G
- STO-3G
- STO-6G
- STO-3G(d)-polarized version of STO-3G

2.4.2. 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-valance basis sets are:
• 3-21G
• 3-21G(d)-polarised
• 3-21+G-diffuse functions.
• 3-21+G(d)-with polarization and diffuse function
• 6-31G
• 6-31G(d)
• 6-31+G(d)
• 6-31G(3df,3pd)
• 6-311G
• 6-311G(d)
• 6-311+G(d)
• 6-311++G(d,p)
• 6-311+G(d,p)

2.4.3. 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.

2.5. GAUSSVIEW

GAUSSVIEW is an affordable, full-featured graphical user interface for GAUSSIAN 09W. 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 GAUSSVIEW to write a molecular structure for the calculation. GAUSSVIEW incorporates an excellent Molecule Builder. One can use it to rapidly 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. GAUSSVIEW 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.

2.6. SCALING OF FORCE FIELDS

SQM, the method of scaled quantum mechanical force fields [67], 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 are 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 [68-70]. 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 were proposed to account for the deviation of the calculated and the observed frequencies. 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., [67] introduced a formula for the scaling of a force constant $f_{ij}$:

$$f'_{ij} = \sqrt{s_is_jf_{ij}}$$

... (2.3)

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.

2.7. NORMAL COORDINATE ANALYSIS

The procedures outlined by Wilson et al., [71,72] Nakamoto et al., [12] and Colthub et al., [56] have been applied in the present investigations for the treatment of normal coordinate analysis of aromatic and heterocyclic compounds.
2.7.1. 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.

2.7.2. 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 are determined.

2.7.3. 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 normalised and orthogonalised.

If $R$ is a column matrix consisting of the internal coordinates and $r$ is the column matrix of the Cartesian coordinates, then

$$ R = Br $$

where $B$ is the transformation matrix of the order $(3N-6) \times 3N$, $N$ being the number of atoms in the molecule. If $U$ is the orthogonal transformation matrix and $S$ is a column matrix of the symmetric coordinates, then

$$ S = UR $$
2.7.4. Potential energy matrix

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

\[ 2V = \sum_i f_i r_i \]

where \( f_i \) are the force constants. This equation can be written in the matrix form as,

\[ 2V = R' FR \]

which becomes in terms of symmetric co-ordinates as,

\[ 2V = S' FS \]

where,

\[ F = U' F U \quad \ldots (2.4) \]

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

2.7.5. Kinetic energy matrix

The kinetic energy can be expressed in the form

\[ 2T = S' G^{-1} S \]

where \( S' \) is the derivative \( \frac{\partial S_i}{\partial t} \) of the \( j^{th} \) internal coordinate. \( G' \) is the inverse kinetic energy matrix obtained from \( B \) matrix.

\[ G = BM^{-1} B' \quad \ldots (2.5) \]

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

2.7.6. Secular equations

After evaluation the elements of potential and kinetic energy matrices, the secular equation.
\[ |FG - E\lambda| = 0 \quad \text{... (2.6)} \]

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
\[
\lambda_k = 4\pi C^2 v_k^2 \quad \text{... (2.7)}
\]

### 2.7.7. 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 factorised into a non-singular matrix such that
\[
G = PP'
\]

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.

\[
W = P' FP
\]

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.
2.8. CALCULATION OF HARMONIC FORCE FIELDS BY MOLVIB

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, 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 Schachtschneider in the 1960’s [73]. Gwinn developed a program for normal coordinate analysis using mass-weighted cartesian coordinates [74], which eliminates the redundancy problems arising when internal valance coordinates are used as in Wilson’s GF method. MOLVIB [75, 76], 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 [77]. 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 polarisation 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 MOLIVB, three methods are available for the scale factor calculations. In two of these methods, the non diagonal terms in the potential energy will depend nonlinearly on the scale factors as,

\[
2V = \sum_i S_i f_{ij} q_i q_j + \sum_i \sum_{j \neq i} \sqrt{S_i S_j} f_{ij} q_i q_j \quad \ldots (2.8)
\]

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 [78]. 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.
2.9. INTENSITY CALCULATIONS IN MOLVIB

The integrated molar absorption coefficient $A_k$ of the $k^{th}$ vibrational mode, $Q_k$ can be expressed as

$$A_k = \frac{1}{4\pi \varepsilon_0} \frac{N_A \pi}{3c^2} \sum \frac{\partial \mu}{\partial Q_k} \left( \frac{\partial \mu}{\partial Q_k} \right)^2 = 974.86277 \sum \left| \frac{\partial \mu}{\partial Q_k} \right|^2 \text{[km/mol]} \quad \ldots (2.9)$$

where the dipole derivatives are expressed in units of eu$^{1/2}$ (summation is over the components of degenerate vibrations).

The components of the derivatives $\frac{\partial \mu}{\partial Q_k}$ are found from [79]

$$\frac{\partial \mu_i}{\partial Q_k} = \sum \frac{\partial \mu_i}{\partial x_\beta} \frac{u_{i\beta}}{\sqrt{m_\beta}} \quad \ldots (2.10)$$

where $\frac{\partial \mu_i}{\partial Q_k}$ are the Cartesian dipole derivatives, obtained from the Gaussian archive file. In the archive file, the dipole derivatives are listed in such an order that the components with respect to the space-fixed coordinates are changing most rapidly. The transition moments are also calculated from the dipole derivatives with respect to the normal coordinates.

In a similar way the polarizability derivatives with respect to the normal coordinates $Q_k$ are found from the Cartesian polarizability derivatives [80]

$$\frac{\partial \alpha_{ij}}{\partial Q_k} = \sum \frac{\partial \alpha_{ij}}{\partial x_\beta} \frac{U_{i\beta}}{\sqrt{m_\beta}} \quad \ldots (2.11)$$

The mean polarisability is calculated from

$$\bar{\alpha} = \frac{1}{3} \sum \left( \frac{\partial \alpha_{11}}{\partial Q_k} + \frac{\partial \alpha_{22}}{\partial Q_k} + \frac{\partial \alpha_{33}}{\partial Q_k} \right)$$
and the anisotropy is found from

\[ \gamma^2 = \frac{1}{2} \left\{ \left( \frac{\partial a_{11}}{\partial Q_k} - \frac{\partial a_{22}}{\partial Q_k} \right)^2 + \left( \frac{\partial a_{11}}{\partial Q_k} - \frac{\partial a_{13}}{Q_k} \right)^2 + \left( \frac{\partial a_{22}}{Q_k} - \frac{\partial a_{13}}{Q_k} \right)^2 \right\} + 6 \left( \frac{\partial a_{12}}{\partial Q_k} \right)^2 + \left( \frac{\partial a_{13}}{\partial Q_k} \right)^2 + \left( \frac{\partial a_{23}}{\partial Q_k} \right)^2 \]

The Raman activity can then be expressed as

\[ \left( \frac{a_0}{\lambda} \right)^4 (45\bar{a}^2 + \gamma^2) = 0.0784163 (45\bar{a}^2 + \gamma^2) \]

... (2.12)

and the depolarization degree as

\[ \rho = \frac{3\gamma^2}{45\bar{a}^2 + 4\gamma^2} \]

... (2.13)

MOLVIB expresses the infrared and Raman intensities in the same units as the GAUSSIAN program.