Chapter II

Quantum Chemical Calculations and Normal Coordinate Analysis
CHAPTER II
QUANTUM CHEMICAL CALCULATIONS AND
NORMAL COORDINATE ANALYSIS

2.1. INTRODUCTION

The philosophy of computational methods of vibrational spectroscopy has changed significantly when quantum mechanical programs for optimization of the geometry of a molecule and for analytical determination of its force field appeared. Harmonic force fields derived from quantum mechanics are widely used at present for the calculation of frequencies and the modes of normal vibrations.

Moreover, in numerous current quantum-mechanical calculations vibrational spectra performed at different levels of approximation, calculated frequencies are, as a rule, higher than their experimental counterparts. This outcome is due to the more or less systematic overestimation of the force constants in the Hartree-Fock method [64]. This overestimation of the force constants depends on the basis set employed [65] and to the not-so-regular discrepancies in applications of the Moller-Plesset theory [66]. These calculations required empirical corrections. To improve agreement with experiment, quantum-mechanical force fields are corrected in one way or another, e.g. using empirical corrections called scale factors, which are estimated from the experimental vibrational spectra of small molecules with reliable frequency assignments.

Second-order Moller-Plesset perturbation theory (MP2) cannot fully take the correlation energy of a system into account (the more so when restricted basis sets are used). Thus, using this theory does not obviate the necessity of scaling force constants. Moreover, with some molecules containing heteroatoms [67], especially halogens [68, 69], this approximation leads to irregular deviations of calculated frequencies from experiment.
Nowadays, sophisticated electron correlation calculations are increasingly available and deliver force fields of high accuracy for small polyatomics. The scaled quantum mechanical force fields [70] are of comparable accuracy with the best purely theoretical results. In addition, the scaling procedure fits the force field to observed (anharmonic) frequencies. Thus, the reproduction of observed spectra will be better with an SQM force field than with the best 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 have to be optimized for energy minimization. Energy minimization is usually performed by gradient optimization i.e., the atoms are allowed to move inorder to reduce the net force on them. The energy minimized structure has small forces on each atom and therefore serves as an excellent starting point for molecular dynamics simulations.

Molecular mechanics deals with the changes in the electronic energy of the molecule due to bond stretching ($V_b$), bond angle bending ($V_q$), out-of–plane bending ($V_{0q}$), internal rotation (torsion) about bonds ($V_F$), interactions between different kinds of motions ($V_{int}$), vander Waals attractions and repulsion between non-bonded atoms ($V_{dw}$) and electrostatic interactions between atoms ($V_{es}$). The sum of these contributions gives the potential energy $V$ in the molecular mechanics framework 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:
\[ V(X^N) = \sum_{i=1}^{k} V_i \quad \ldots (2.1) \]

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 parameters of the energy functions must be known in advance for all types of energy terms comprising the molecular systems.

The equation (2.1) can be written as,

\[ V = V_b + V_q + V_F + V_{eq} + V_{ez} + V_{dv} + V_{in} \quad \ldots (2.2) \]

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 finds the nearest local energy minimum by minimizing the steric energy \( V \) of the equation (2.2). This equation provides as analytical form for the energy, the first and second derivatives of \( V \) can easily be evaluated analytically, which facilitates the energy minimization. Many programs have built-in searching methods that locate many low energy conformers. 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 in full or in part on 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, which depend on second derivatives. Frequency calculations are not possible or practical for all computational chemistry methods.

2.2.1 Molecular Mechanics

Molecular mechanics simulations use the laws of classical physics to predict the structures and properties of molecules. There are different molecular mechanics methods. Each one is characterized by its particular force field. These classical force fields are based on empirical results, averaged over a large number of molecules. Because of this extensive averaging, the results can be good for standard systems; no force field can be generally used for all molecular systems of interest. However, molecular mechanics methods cannot describe bond formation or bond breaking or predict molecular properties which depend on molecular orbital interactions.

2.2.2 Electronic Structure Methods

Electronic structure methods use the law of quantum mechanics as the basis for their computations. Quantum mechanics states that the energy and the other related properties of a molecule can be obtained by solving the Schrodinger equation,

\[ H \psi = E \psi \]  \hspace{1cm} \text{... (2.3)}
However, exact solutions to the Schrodinger equation are not practical. Electronic structure methods are characterized by their various mathematical approximations to their solutions. There are two major classes of electronic structure methods:

- Semi-empirical methods use a simpler Hamiltonian than the correct molecular Hamiltonian and use a parameter whose values are adjusted to fit the experimental data. That means they solve an approximate form of the Schrodinger equation that depends on having approximate parameters available for the type of chemical system in question. There is no unique method for the choice of parameter. Ab initio force fields provide solutions to these problems.

- Ab initio methods use the correct Hamiltonian and does not use experimental data other than the values of the fundamental physical constants (i.e., c, h, mass and charges of electrons and nuclei). Moreover, it is a relatively successful approach to perform vibrational spectra.

2.3. 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 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 give 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 theory (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 [71-74] have evolved as a powerful quantum chemical tool for the determination of the electronic structure of molecules. In the framework of DFT approach, different exchange and correlation functional are routinely used. Among these, the Becke-3-Lee-Yang–Parr (B3LYP) combination [75, 76] is the most used since it has 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 between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The vibrational frequencies calculated by applying DFT methods are normally more 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 applying empirical corrections called scaling, where the empirical scaling factors are ranging from 0.8 to 1.0. The scaling factors depend both on method and basis sets and they are partially compensate for the systemic errors in the calculation of frequencies. Global scaling or uniform scaling, multiple scaling or selective scaling are some scaling methods advocated to minimize the overestimation of
the frequency differences. Ab initio calculation could be performed using Gaussian 98W Software package [77].

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 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 [78-80].

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

```
Graphical input of geometry
Or
Input files as recommended by Gaussian inc.

Ab initio geometry optimizations including offset forces

Cartesian gradient, Force constant, Dipole moment and Polarisability derivatives

Transformation of force constants, Dipole moment and polarisability derivatives, scaling of F, Normal coordinates analysis

Theoretical frequencies and IR, Raman intensities in the form of graphical display
```

**Fig. 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 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 electron wave function. The main objective of density functional theory is to replace the many-body electronic wave functions 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 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, e.g., 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 or clusters are seen as fixed (the Born-Oppenheimer approximation), generating a static external potential \( V \) in which the electrons are moving. A stationary electronic state is then described by wave functions \( \Psi(r_1,...,r_N) \) fulfilling the many–electron Schrödinger equation.

\[
H \Psi = [T + V + U] \Psi = \left[ \sum_i \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_i V(r_i) + \sum_{i<j} U(r_i, r_j) \right] \Psi = E \Psi \quad \ldots (2.4)
\]

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 so called universal operators as they are the same for any system, while \( V \) is system dependent or non-universal. As one can see, the actual difference between a single particle problem and the much more complicated many-particle problem just 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 the huge computational effort, which makes it virtually impossible to apply them efficiently to larger, 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 \( U \), into a single-body problem without \( U \). In DFT the key variable is the particle density \( n(r) \) which is given by,

\[
n(r) = N \int d^3 r_2 \int d^3 r_3 \ldots \int d^3 r_N \Psi^*(\vec{r},\vec{r}_2,...,\vec{r}_N) \Psi(\vec{r},\vec{r}_2,...,\vec{r}_N) \quad \ldots (2.5)
\]
Hohenberg and Kohn proved in 1964 [81] that the relation expressed above can be reversed, i.e., to given ground state density $n_0(\vec{r})$ it is in principle to calculate the corresponding ground state wave function $\Psi_0(\vec{r},...\vec{r}_N)$. In other words, $\Psi_0$ is a unique functional of $n_0$, i.e.,

$$\Psi_0 = \Psi_0[n_0]$$

... (2.6)

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

$$\langle O[n_0] = \langle \Psi_0[n_0]|O|\Psi_0[n_0]\rangle$$

...(2.7)

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

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

... (2.8)

where the contribution of the external potential $\langle \Psi_0[n_0]|V|\Psi_0[n_0]\rangle$ can be written explicitly in terms of the density.

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

...(2.9)

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

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

... (2.10)

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

The variational problem of minimizing the energy functional $E[n]$ can be solved by applying the Lagrangian method of undetermined multipliers,
which was done by Kohn and Sham in 1965 [83]. The functional in the equation (2.10) can be written as a fictitious density functional of a non-interacting system.

\[ E_s[n] = \langle \Psi_s[n] | T_s + V_s | \Psi_s[n] \rangle \] ... (2.11)

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

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

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

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \] ... (2.12)

which yields the orbitals \( \phi_i \) that reproduce the density \( n(\vec{r}) \) of the original many-body system.

\[ n(\vec{r}) \equiv n_s(\vec{r}) = \sum_i N_i \left| \phi_i(\vec{r}) \right|^2 \]

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

\[ V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r + V_{xc} [n(\vec{r})] \] ... (2.13)

where the second term of equations (2.13) denotes Hartree term describing the electron-electron Coulomb repulsion, while the last term \( V_{xc} \) is called the 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 $\phi$, which in turn depends on $V_s$, the problem of solving the Kohn-Sham equation has to be done in a self-consistent (i.e., iterative) way. Usually, one starts with an initial guess for $n(r)$, then calculated the corresponding $V_s$ and solves the Kohn-Sham equations for the $\phi$. 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 [75, 76, 83] which is a hybrid method in which the DFT exchange functional is combined with the exchange functional from Hartree–Fock theory. These hybrids functional carry adjustable parameters, which are generally fitted to a training set of molecules.

### 2.5 BASIS SET

Modern quantum chemical calculations are typically performed within a finite set of basis functions. Gaussian 98 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 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 hug 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.

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 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 are 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 functions. In these basis sets, the same number of Gaussian primitives comprises core and valence 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 Valence 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 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 hypens 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* - polarized
• 3-12+g – Diffuse functions
• 3-12+g *-with polarization and diffuse function
• 6-31g
• 6-31g*
• 6-31+g*
• 6-31g (3dt,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- PVDZ- 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 polarised’ 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. GAUSSVIEW

Gaussview is an affordable, full-featured graphical user interface for Gaussian 98. With the help of Gaussview, one can prepare input for submission to Gaussian and 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.

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.
- Animation of the steps in geometry optimizations, potential energy surface scans, intrinsic reaction coordinate (IRC) paths, and molecular dynamics trajectories from BOMD and ADMP calculations.
2.7. SCALING OF FORCE FIELDS

SQM, the method of scaled quantum mechanical force fields [75] is a pragmatic approach to the ab initio based determination of molecular force fields. Its basic 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 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 [84 -86]. 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 [87]. 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. [75] introduced a formula for the scaling of a force

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

...(2.14)

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.

2.8. 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 preferably the 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.
2.8.1 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.

2.8.2 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.

2.8.3 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 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 \( S = UR \)

2.8.4 Removal of Redundant Coordinates

The number of internal coordinates must be equal to or greater than \( \frac{3n-6}{3n-5} \) degrees of vibrational freedom of molecule containing \( n \) atoms. If more than \( \frac{3n-6}{(3n-5)} \) 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 a 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 dropout as zero roots of the secular equation when the symmetrized kinetic energy matrix is diagonalized.

### 2.8.5 Potential Energy Matrix

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

$$2V = \sum_{ij} f_{ij} r_{ij}$$

where $f_{ij}$ are the force constants. This equation can be written in the matrix form as,

$$2V = R' FR$$

which becomes in terms of symmetric coordinates as,

$$2V = S' FS$$

where,

$$F = U' FU$$

$R', S'$ and $U'$ are the transposes of $R$, $S$ and $U$ - matrices respectively.
2.8.6 Kinetic Energy Matrix

The kinetic energy can be expressed in the form

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

where \( S' \) is the derivative of the \( j^{\text{th}} \) internal coordinate, \( G^{-1} \) is the inverse kinetic energy matrix obtained from the \( B \)-matrix

\[ G = BM^{-1}B' \]

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

2.8.7 Secular Equations

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

\[ |FG - E\lambda| = 0 \]

is to be solved for evaluating the potential energy constants.

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

\[ \lambda_k = 4\pi C^2 v_k^2 \]

2.8.8 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 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.

### 2.8.9 Computation of L Matrix

L-Matrix is obtained from the force field by factorising the symmetrised $G$ - matrix into a product of triangular matrices $T$ and $T'$

$$ G = PP'F $$
$$ G = LL' $$
$$ L = PO $$

where $O$ is an orthogonal matrix

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

$$ LFL = \Lambda $$
$$ P'O'FPO = \Lambda $$
$$ O'(P'FP)O = \Lambda $$
$$ O'WO = \Lambda $$

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.
2.8.10 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 \( 4\pi^2 c^2 v_a^2 \)

2.9. SCALING OF AB INITIO 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, 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 1960s [88]. Gwinn developed a program for normal coordinate analysis using mass-weighted Cartesian coordinates [89], which eliminates the redundancy problems arising when internal valance coordinates are used as in Wilson’s GF-method. Molvib [90, 91], a Fortran program is based on the above idea developed for the calculation of harmonic force fields and vibrational modes of molecules 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 [92]. 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,

\[ 2V = \hat{A}_i S_i f_i q_i q_j + \hat{A}_j \sqrt{S_j S_i} f_i q_i q_j \]  

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 [87]. However, too many different scale factors should not be used in this case, 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.

2.9.1 Intensity Calculations in Molvib

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

\[
A_k = \frac{1}{4\pi \varepsilon_0} \frac{N_k \pi}{3c^2} \sum_{g} \left| \frac{\partial \mu}{\partial Q_k} \right|^2 = 974.86277 \sum_{g} \left| \frac{\partial \mu}{\partial Q_k} \right|^2 \text{[km/mol]}
\]

where the dipole derivatives are expressed in units of eu^{½} (summation is over the components of degenerate vibrations). The components of the derivatives \( \frac{\partial \mu}{\partial Q_k} \) are found from [150].

\[
\frac{\partial \mu_i}{\partial Q_k} = \sum_{\beta} \frac{\partial \mu_i}{\partial X_\beta} \frac{u_{\beta k}}{\sqrt{m_\beta}}
\]

where \( \frac{\partial \mu_x}{\partial Q_k} \) 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 [151].

\[
\frac{\partial \alpha_{ij}}{\partial Q_k} = \sum_p \frac{\partial \alpha_{ij}}{\partial x_p} \frac{U_{pk}}{\sqrt{m_p}}
\]

The mean polarisability is calculated from

\[
\bar{\alpha} = \frac{1}{3} \sum_k \left( \frac{\partial \alpha_{11}}{\partial Q_k} + \frac{\partial \alpha_{22}}{\partial Q_k} + \frac{\partial \alpha_{33}}{\partial Q_k} \right)
\]

and the anisotropy is found from

\[
\gamma^2 = \frac{1}{2} \left\{ \left( \frac{\partial \alpha_{11}}{\partial Q_k} - \frac{\partial \alpha_{22}}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_{11}}{\partial Q_k} - \frac{\partial \alpha_{33}}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_{22}}{\partial Q_k} - \frac{\partial \alpha_{33}}{\partial Q_k} \right)^2 \right\}
\]

\[
+ 6 \left\{ \left( \frac{\partial \alpha_{12}}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_{13}}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_{23}}{\partial Q_k} \right)^2 \right\}
\]

The Raman activity can then be expressed as

\[
\left( \frac{\alpha_0}{\bar{\alpha}} \right)^4 (45\bar{\alpha}^2 + \gamma^2) = 0.0784163(45\bar{\alpha}^2 + \gamma^2)
\]

and the depolarization degree as

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

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