INTRODUCTION – VIBRATIONAL SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

Infrared spectroscopy is certainly one of the most important analytical techniques available to today’s scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state may be studied. Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be examined with a judicious choice of sampling technique. As a consequence of the improved instrumentation, a variety of new sensitive techniques have now been developed in order to examine formerly intractable samples. Spectroscopy is now the best analytical tool for a chemist to elucidate and establish molecular structure. Among them the Vibrational spectroscopy is the most valuable for elucidating the molecular structure and characteristics of organic, inorganic, co-ordination compounds and polymers. With the help of the vibrational spectroscopy it is possible to study the intramolecular forces acting between the atoms in the molecule, the intermolecular forces or the degree of association in condensed phases and in the determination of molecular symmetries. In addition to the above it helps in the identification of functional groups or compound identification, determination of nature and strength of the chemical bond and the calculation of thermodynamic properties.

It is important for us to distinguish between molecular vibrations in which molecular coordinates are deformed, and lattice vibrations in which the atoms vibrate around their equilibrium position in the crystal lattice. For elements and many binary materials all vibrations are lattice vibrations - there are no molecules. For molecular solids the forces holding the atom of the molecule together are much stronger than the forces holding the molecules within the lattice, so in this case low-energy vibrations in which the whole molecule is displaced are termed “lattice” (or external) vibrations. The higher frequency vibrations that distort the molecule are then molecular (or internal) vibrations. There is usually some separation between the frequency region of the internal and external vibrations, but sometimes a “soft” internal vibration such
as torsion may arise at a frequency that is below some of the external vibrations. Coupling between the internal vibrations of neighbouring molecules is usually weak and it is common to analyse the molecular vibrations as if the molecule were isolated, or in the gas-phase.

Vibrations probe the potential energy surface of all the atoms in a molecule in all directions. They therefore measure the forces holding the atoms of a molecule together, and the forces holding the molecule in the crystal. Further, when a bond is stretched the electron distribution in the molecule is altered which in turn affects how easy it is to deform the molecule in some other way at the same time. It is thus an ideal probe for understanding inter and intra-molecular forces and interactions between these. Sometimes molecules are very flexible and will deform even in a small external force. Although the total potential energy is virtually unchanged, the change in molecular geometry changes the characteristic vibrations of the molecule.

In the absence of crystallographic data, the molecular structure can be derived from the molecular vibrations.

1.1. Infrared Spectroscopy

The absorption of infrared (IR) radiation distorts the dipole of the molecule, inducing molecular vibrations with energy shifts an order of magnitude smaller than in electronic absorption spectra. The transition moment for infrared absorption involves the permanent dipole moment operator, instead of the induced dipole moment operator as in the case of Raman scattering. Therefore the transition probability is proportional to the square of

\[ [\vec{P}]_{fi} = \langle f | \vec{P} | i \rangle \]  

where \( \vec{P} \) is the electric dipole moment operator. It can be shown that the transition moment has the same transformation properties as

\[ \langle f | x | i \rangle, \langle f | y | i \rangle \text{ and/or } \langle f | z | i \rangle \]  

(1.2)

Thus, the infrared activity of a non–degenerate fundamental vibration \( Q_j \) requires, product of the type \( Q_jx, Q_jy \) or \( Q_jz \) to be totally symmetric. That is, the fundamental vibrational modes, which are in the same symmetry species with \( x, y \) or \( z \) vectors are infrared active.
1.2. Fourier transform Infrared (FTIR) Spectroscopy

1.2.1. Theory and Instrumentation

Fourier transform infrared (FTIR) spectroscopy is an interference technique uses the Michelson interferometer as the multiplex optical device [1]. The building blocks of all FTIR instrument have the chain:

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SOURCE → INTERFEROMETER → SAMPLE → DETECTOR
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1.2.2. Source

The commonly used radiation source is globar operating on the basis of the black body radiation. It consists of a SiC (silicon carbide) with dimensions 2 cm in length and 0.5 cm in diameter heated to about 1450 K. The globar is generally used in the spectral range up to 100 µm and operated in vacuum only. Nernst glower (sintered mixtures of the oxides of Zr, Th, Ce, Y, and Er) is also used as source in some spectrometers depending upon the spectral range. Besides thermic sources semiconductor lasers are also used in FIR, MIR and NIR regions. Microwave generators like kelstrons or magnetrons are also used for wide frequency range.

1.2.3. Interferometer

The interferometer is the bit that analyses the infrared or near infrared and hence enable us to generate the spectrum. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. The beam splitter is the crystal of potassium bromide coated with germanium [2], splits the incident light equally reflecting half to the stationary mirror while transmitting the other half to the moving mirror. The white light from the source located at the focus of lens is separated into two parts by the beam splitter. The reflected part is focused onto the detector after reflection from the stationary mirror and after a second split by the beam splitter. The transmitted part of the light is also focused onto the detector after it was reflected from the moving mirror and split again by the beam splitter. The moving mirror can glide a very short distance $\Delta x$ (typically
a few millimeters). The schematic diagram of classic Michelson interferometer is shown in Figure 1.1, contain a source, detector, stationary and moving mirrors and a beam splitter.

Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. In this way interference fringes develop at the detector. Their intensity $I(x)$ depends on the position $x$ of the moving mirror. $I(x)$ is termed interferogram function. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured; all frequencies are being measured simultaneously.

![Figure 1.1. Schematic diagram of Michelson interferometer](image)

Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. A means of “decoding” the individual frequencies can be accomplished via a well–known mathematical technique called the Fourier
transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis [3].

1.2.4. Detectors

The commonly used system is the Golay detector, which works under a pneumatic principle. A thin film absorbs the incident IR light. The generated heat increases the pressure in the gas chamber, which drives a mirror. The mirror is a part of an optical system that images a grating onto itself. Any small motion of the mirror leads to a change in the overlap between grating and the image and thus gives a signal to the detector. The layout of Bruker IFS 66V spectrometer used to record FTIR and FT–Raman spectra in the present work is shown in Figure 1.2.

Figure 1.2. Layout of Brucker IFS 66V Fourier transform spectrometer

1.3. Advantages of FTIR Technique

✓ Higher signal–to–noise due to improved detector irradiance.
✓ Higher energy throughput because no slits are required.
✓ Accurate wavelength measurements due to calibration with an internal laser.
✓ High speed as interferometers can be more rapidly scanned than monochromators. It provides a series of quick scans (10 per sec) so that it can be used ‘on the fly’ e.g. for transient samples or chromatography eluates.

✓ Signal–to–noise ratio can be improved by signal averaging, thereby giving better resolution and/or facilitating examination of much smaller samples.

✓ It captures all frequencies at once and simultaneously records the full spectrum.

✓ Spectral resolution can be adjusted from 0.5 to 16 cm\(^{-1}\) to the application.

1.4. Raman Spectroscopy

The scattering of monochromatic radiation that is incident on a sample can tell the Raman spectroscopist something of the sample's molecular structure. If the frequency (wavelength) of the scattered radiation is analysed, not only is the incident radiation wavelength observed via elastic scattering (Rayleigh scattering), but also a relatively small amount of radiation is scattered inelastically at some different wavelengths, referred to as stokes and anti–stokes Raman scattering. Approximately only \(1 \times 10^{-7}\) of the scattered light is inelastically scattered Raman. The scattered radiation occurs in all directions and may also have observable changes in its polarization along with its wavelength. It is the shift in wavelength of the inelastically scattered radiation that provides the chemical and structural information. Raman shifted photons can be of either higher or lower energy, depending upon the vibrational state of the molecule under study. Stokes radiation occurs at lower energy (longer wavelength) than the Rayleigh radiation, and anti–stokes radiation has greater energy. The energy increase or decrease is related to the vibrational energy levels in the ground electronic state of the molecule, and as such, the observed Raman shift of stokes and anti–stokes features are a direct measure of the vibrational energies of the molecule. The energy of the scattered radiation is less than the incident radiation for stokes line and the energy of the scattered radiation is more than the incident radiation for the anti–stokes line. The anti–stokes line is much less intense than stokes line. This occurs because only molecules that are vibrationally excited prior to irradiation can give rise to the anti–stokes line. Hence, in Raman spectroscopy, only the more intense stokes line is normally measured.
If the molecule is initially at state $|i\rangle$ with the energy $E_i$ and after interaction with the monochromatic radiation of angular frequency $\omega_0$ goes to state $|f\rangle$ with energy $E_f$, from the conservation of energy,

$$E_i + \hbar \omega_0 = E_f + \hbar (\omega_0 \pm \omega_{fi})$$  \hspace{1cm} (1.3)

where, $\hbar \omega_{fi} = E_f - E_i$ and $\hbar (\omega_0 \pm \omega_{fi}) = \hbar \omega_s$, the energy of the scattered photon.

If $E_f > E_i$, $\omega_s = (\omega_0 - \omega_{fi})$ Stokes \hspace{1cm} (1.4)

If $E_f < E_i$, $\omega_s = (\omega_0 + \omega_{fi})$ Anti-stokes \hspace{1cm} (1.5)

The stokes lines are more intense than the anti–stokes lines, a consequence of the different populations of molecules in the ground and first excited vibrational states, as described by the Boltzmann distribution.

In quantum theory of scattering, the intensity arising from a transition between states $|i\rangle$ and $|f\rangle$, under ordinary conditions of Raman scattering experiments, depends on the polarisability tensor, $[\alpha_{xy}]_{fi}$. For a particular transition to be Raman active, at least one of the tensor components of $[\alpha_{xy}]_{fi}$ must be non–zero.

### 1.5. Depolarisation Ratio

One of the most useful pieces of information that one can obtain from Raman spectra is the depolarization ratio ($\rho$) of a vibrational mode. The value of this ratio gives an indication as to the symmetry of vibrational mode and thus is invaluable in making band assignments. The procedure uses the polarized incident laser light and analyses the scattered light for that component with polarization parallel to $(I_{\parallel})$ and perpendicular to $(I_{\perp})$ the polarization of the incident light. The state of polarisation of the Raman scattering is shown in Figure 1.3 which yields valuable information concerning the molecular vibrations. An aspect of the Raman spectrum that differs fundamentally from the infrared is the ability to observe bond polarisation in liquids and gases where the molecules are randomly oriented. Since in a typical Raman experiments the scattering molecule is rotating, the observed scattering will be the average of all orientations of the molecule. To express the scattering intensity in terms of the derived polarisability tensor, it is necessary to find quantities which are invariant under rotation.
It is possible to express these invariants in terms of two quantities associated with the tensor, Mean value $\alpha' = 1/3 (\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz})$ and $\gamma'=1/2 (\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{yy} - \alpha'_{zz})^2 + (\alpha'_{zz} - \alpha'_{xx})^2 + 6(\alpha'_{xy}^2 + \alpha'_{yz}^2 + \alpha'_{zx}^2)$ (1.7)

where, $\alpha'_{ij} = (\delta \alpha_{ij}/\delta Q)_0$. Then for $90^\circ$ scattering, the depolarisation ratio $\rho_n$ representing the ratio of intensities scattered perpendicular and parallel to the direction of the electric vector $E$ is given by

$$\rho_n = 6\gamma'^2 / (45\alpha'^2 + 7\gamma'^2)$$

Using plane polarised incident radiation, such as for laser radiation

$$\rho_p = 3\gamma'^2 / (45\alpha'^2 + 4\gamma'^2)$$

If $\rho_p = 0.75$, then the line is said to be depolarised; if $\rho_p < 0.75$, the line is polarised and $\rho_p = 0$, the line is completely polarised.

For the symmetric vibrations, the size of the ellipsoid changes but its orientation does not. That is, the change in diagonal elements of the polarisability ellipsoid implies that $\alpha'$ changes and hence the line must be polarised i.e., $\rho_p < 0.75$. Antisymmetric vibrations, on the other hand do not lead to a change in the size and hence $\alpha'$. Hence Raman lines due to antisymmetric vibrations are depolarized. Information of this type can be of great use in determining the symmetry of vibrations.
1.6. Mutual Exclusion Rule

For molecules with centre of symmetry, transitions that are allowed in the Raman spectrum are forbidden in infrared and conversely, transitions that are allowed in the infrared spectrum are forbidden in Raman. That is in Raman effect, only transitions between states of same symmetry with respect to the centre of symmetry (\(i\)), can takes place (\(g \leftrightarrow g, u \leftrightarrow u\)), however in the infrared, only transition between the states of opposite symmetry with respect to the centre of symmetry are allowed (\(g \leftrightarrow u\)).

1.7. FT–Raman Spectroscopy

In conventional Raman spectroscopy, the strongly interfering fluorescence has always been a great nuisance and obscures the Raman signal. The introduction of FT–Raman spectroscopy has brought a new impetus to Raman spectroscopy. It has allowed the study of materials that were previously “impossible” because of fluorescence [4–6] and provides ready access in the extensive data handling facilities that are available with a commercial FTIR spectrometer. Thus, Raman spectroscopy is taking its place as an equal partner in vibrational spectroscopy.

Fluorescence can be avoided by using an excitation frequency below the threshold for any fluorescence process. The most common excitation frequency for FT–Raman spectroscopy is the Nd:YAG (Neodymium doped Yttrium Aluminium Garnet) laser source of wavelength 1.064 \(\mu\)m, where there is no electronic transitions and hence fluorescence can be eliminated. A further advantage is that at these low photon energies, sample heating and subsequently photochemical sample degradation are unlikely.

Consequently, the Raman scattering occurs in the near–IR region, and conventional FTIR instrumentation can be used with modification. FT–Raman also benefits from advantages inherent to interferometry: high resolution efficiency, excellent wavelength precision, easily variable resolution, spectral coverage, higher optical throughput and software developments in FTIR.

FT–Raman samples typically require no preparation and the analysis is non–destructive, saving time by eliminating sample preparation or alignment of sampling geometries [7]. Another advantage is that glass is transparent to the near–infrared radiation used in the FT–Raman technique, allowing a wide variety of cells to be constructed easily and cheaply.
1.8. FT–Raman Instrumentation

Recent advances in instrumentation have considerably eased the task of converting an FTIR spectrometer (with NIR capacity) to carry out the FT–Raman experiment and achieve signal–to–noise ratios comparable with those obtainable conventionally [8, 9]. The schematic diagram of FT–Raman spectrometer is shown in Figure 1.4.

The FT–Raman instrument has the following accessories:

(i) a near IR laser excitation source (typically Nd:YAG at 1.064 µm).
(ii) a Fourier transform interferometer equipped with the appropriate beam splitter (quartz).
(iii) a sample chamber with scattering optics that match the input port of the Fourier transform instrument.
(iv) a set of optical filters for rejection of the Rayleigh scattered light.
(v) a low noise detector (InGaAs or Ge) for the near IR region/pre–amp.

![Figure 1.4. Schematic diagram of FT–Raman spectrometer](image)

Since all of scattered radiation from the sample is collected and Fourier transformed in the FT–Raman experiment, a Rayleigh line filter is used. There are two main techniques for the removal of this light: Rejection filters–dielectric filters, the optical notch filter or colored glass filters minimises the amount of Rayleigh scattered light entering the interferometer and is essential for FT–Raman spectroscopy [6]. Subtractive Double Spectrographs – a double spectrograph functioning in
subtractive mode is often used as Rayleigh filter. This is typically followed by a single dispersive spectrograph. The sharpness of the cutoff determines the low frequency limit of the FT–Raman spectrometer.

The detector is the liquid nitrogen–cooled high sensitive Indium Gallium Arsenide (InGaAs) detector with specially configured preamplifier required for the low levels of collected radiation typical in Raman experiment. A focusing lens is inserted in the accessory to provide a laser spot size at the sample approximately equal to output beam waist of the laser. The use of attenuators may be necessary where the sample of interest is a very strong scatterer or a sample which has a tendency to heat up with the incident laser energy. Typically, a visible He:Ne laser beam is co–aligned with the invisible Nd:YAG laser beam to make it possible to align and focus the Nd:YAG beam. A schematic diagram of Nd:YAG laser, pumped by an arc lamp or diode laser array is given in Figure 1.5. Another option is to use fiber optics [10]. With fiber optic components, optical alignment is virtually eliminated which allows rapid switching from one sample to another. Recently, Ti:Sapphire laser which excite at 1.3 \( \mu \)m show beneficial for further minimisation of fluorescence [11].

![Figure 1.5. Schematic diagram of Nd:YAG laser](image)

In the future, other lasers operating near 900 nm may be used to take advantage of the \( \nu^4 \) gain, while still avoiding the fluorescence problem. For example,
diode lasers have made big progress and are now available with reasonable power levels (30–300 mW) at 785 and 830 nm. Tunable excitation in the region 670–1100 nm can be obtained with Ti:Sapphire laser.

1.9. Advantages of FT–Raman Spectroscopy

FT–Raman enjoys several distinct advantages. They are,

1. The transparency of water and glass: the very low Raman scattering of water (which is important for living systems) and of glass make it suitable for dilute aqueous solutions of substances as well as for hygroscopic materials, and permits the use of standard glass cuvettes and capillaries.


3. Very small amounts of materials can be examined, without modification since the laser beam can be focused down to about a spot with a diameter of 100 μm.

4. Symmetrical bonds such as C–C, C=C, C≡C, N=N, O–O, S–S manifests themselves by giving the most intense bands in Raman spectra, while they are inactive in the infrared.

5. Fiber optics can be used for remote sampling.

6. The decrease in fluorescence which enables the researcher to collect good Raman data from nearly all samples.

7. The wavenumber accuracy of interferometry is exhibited in FT–Raman spectroscopy enabling the analysis to signal average and to perform spectral subtraction.

8. Another advantage is the rate at which the spectra can be acquired. Hence it is a useful tool for the study of kinetic processes such as polymer curing.

9. FT–Raman spectroscopy using FTIR instrumentation solves another problem frequently encountered in conventional spectrometers, which is lack of sufficient frequency precision required to perform the spectral subtractions [12].

1.10. Sampling Techniques in FT–Raman Spectroscopy

A sample in any state can be examined without difficulty by using FT–Raman spectroscopy. The laser beam is narrow, collimated and unidirectional, so it can be
manipulated in a variety of ways depending on the configuration of the sample. For liquids, a cylindrical cell of glass or quartz with an optically flat bottom is positioned vertically in the laser beam. For solids, the particular method used depends on the transparency of the sample. For clear pellets or the samples, right angle scattering is used. Powdered samples can be analysed by using front surface reflection from a sample holder consisting of a hole in the surface of a metal block inclined at 90° with respect to beam. One of the advantages of Raman sampling is that glass containers can be used which can be sealed if desired [13].

1.11. Sampling Methods in FTIR Spectroscopy

Solids are usually examined as a mull, a pressed disc or as deposited glassy films. Mulls are prepared by grinding the solid and then suspending with 1–2 drops of mulling agent followed by further grinding until the suspended particles are less than 2 µm. The mull is then examined as a thin film between flat salt plates. The commonly used mulling agents are Nujol, Hexachlorobutadiene and Volt of 3s oil (halogenated hydrocarbon) depending upon the spectral region.

1.11.1. Alkali halide disc

The solid is mixed with suitable dry alkali halide (100–200 mg) grounded in a mortar or ball mill and subjected to a pressure of about 10 ton/sq. inch in an evacuated dye. This sinters the mixture and produces a clear transparent disc of diameter 10–15 mm. The advantage of this method over mull technique is that it eliminates the problem of bands, which appear due to mulling agent. The most commonly used alkali halide is KBr, which is transparent in the commonly scanning region. The commonly used other alkali halides are NaCl, CsI and CsBr.

1.11.2. Solutions

The sample can be dissolved in a solvent and the spectrum of this solution can be recorded. The solution (usually 5%) is placed in a solution cell, which has path length of usually 0.1–1.0 mm. The solvent chosen must satisfy certain criteria: (i) it has to dissolve the compound (ii) it should be non–polar as possible, to minimise solute solvent interactions (iii) it should not react with the sample (iv) it should not absorb IR radiation (v) it should be volatile and not viscous and (vi) it should be pure and dry. CS₂, CCl₄, CHCl₃, CDCl₃ and C₂H₂Cl₄ are some of the solvents commonly used.
Neat liquids can be examined between salt plates without a spacer. Pressing the liquid sample between flat plates produces a film of 0.01 mm or less in thickness. The plates are held together by capillary action.

1.12. Normal Modes of Vibration

The motion of a molecule of \( n \) atoms is defined by the variation of \( 3n \) coordinates; i.e., molecules possess \( 3n \) degrees of freedom. For simple harmonic motion, a molecule of \( n \) atoms can vibrate in \( 3n-6 \) ways, (or \( 3n-5 \) in the case of linear molecule). These \( 3n-6 \) vibrations are the normal vibrations of the molecule, and the displacements of the atoms from their equilibrium positions are the normal coordinates.

The classical methods of obtaining the normal mode is as follows: Let the position of the systems be represented by the coordinates \( q_1, q_2, q_3, \ldots, q_n \). If the oscillations are regarded as having infinitesimally small amplitudes in comparison with the nuclear distances, both the kinetic and potential energies may be expressed as

\[
2T = \sum_{i=1}^{3n} \dot{q}_i^2 \quad \text{(1.10)}
\]

\[
2V = \sum_{j=1}^{3n} f_{ij} q_i q_j \quad \text{(1.11)}
\]

The \( f_{ij} \) coefficients are called force constants, since they represent the forces acting to restore a displaced atom to its equilibrium for displacement \( q_i \) and \( q_j \). The equations of motion for a vibrating molecule can be obtained from the expression of \( T \) and \( V \). It is convenient to write Newton’s second law of motion with the Lagrange form

\[
\frac{d}{dt} \left[ \frac{\partial T}{\partial \dot{q}_j} \right] + \left[ \frac{\partial V}{\partial q_j} \right] = 0 \quad \text{(1.12)}
\]

If equation (1.12) is applied successively with each coordinate in turn, using equations (1.10) and (1.11) to supply the values of \( T \) and \( V \), there will result a series of simultaneous differential equations. The general solutions of these equations of the form

\[
q_i = A_i \cos(\lambda^{1/2} t + \epsilon) \quad \text{(1.13)}
\]

in which \( \lambda = 4\pi^2 c^2 \nu^2 \), where \( \nu \) is the frequency of vibration in \( \text{cm}^{-1} \) and \( c \) is the velocity of light; \( \epsilon \) is the phase factor and \( A_i \) is the amplitude of vibration of \( i^{th} \) atom. Then from equations (1.12) and (1.13),
\[ \sum_{i=1}^{3n} (f_{ij} - \delta_{ij} \lambda) A_i = 0 \quad j = 1, 2, \ldots, 3N \]  
(1.14)

Apart from the trivial solution \( A_i = 0 \), the solutions are given by the conditions
\[ |f_{ij} - \delta_{ij} \lambda| = 0 \]
(1.15)

The above equation is the secular equation. The values of \( \lambda \), obtained as solutions of secular equations are known as eigen values.

The evaluation of the determinant is simplified by the transformation to a new set of coordinates \( Q_i \), such that the cross product terms in kinetic and potential energy equations disappears. By employing the orthogonal transformation
\[ q_i = \sum_{i=1}^{3n} C_{ij} Q_i \]
(1.16)

upon which, the kinetic and potential energy become
\[ 2V = \sum_{i} \lambda_i Q_i^2 \]
(1.17)
\[ 2T = \sum_{i} \dot{Q}_i^2 \]
(1.18)

This normal coordinate transformation gives, analogously to equation (1.13), the expression
\[ Q_i = B_i \sin(\lambda_i^{1/2} t + \varepsilon') \]
(1.19)

To each value of \( \lambda \) which is a root of secular equation, there corresponds a normal vibration of the molecule in which all coordinates \( Q_i \) vibrate with the same frequency and phase. Thus the atoms attain their positions of maximum displacement simultaneously.

The vibrational problem is much easier to describe by means of matrix algebra. The displacement coordinates are expressed as a column matrix \( X \) and the force constant can be represented as a symmetric square matrix \( F \). The kinetic and potential energies in quadratic form are given by
\[ 2V = X^T F X \]
(1.20)
\[ 2T = \dot{X}^T M \dot{X} \]
(1.21)

where \( M \) is a diagonal matrix. The kinetic and potential energies in mass adjusted coordinates are,
\[ 2V = q^T F_q q \]
(1.22)
\[ 2T = q^T \dot{q} \]
(1.23)
where, $F_q$ is the force constant matrix.

**1.13. Solution of Secular Equation in Internal Coordinates**

By using a set of internal coordinates that describe the bond distortions, such as bond stretching, angle deformations, and torsion, the size of the secular equation in internal coordinate is smaller and hence easier to solve. The linear transformation between Cartesian and internal coordinates in matrix form is $R = BX$, similarly between internal coordinates and mass adjusted coordinates is $R = Dq$, where $B$ and $D$ matrices are related by the expression $D = BM^{-1/2}$. The kinetic energy in terms of mass weighted Cartesian coordinate in matrix form is given by

$$2T = \dot{q}^T \ddot{q}$$  \hspace{1cm} (1.23)

In order to express the kinetic and potential energy in terms of internal coordinates $R$, it is necessary to define a quantity $P$, which is a momentum conjugate to $q$, as $p_j = \dot{q}_j$.

So that, the kinetic energy can be written as

$$2T = p^T p$$  \hspace{1cm} (1.24)

after substituting $p^T = p^T D$, the kinetic energy can be expressed as

$$2T = p^T DD^T p$$  \hspace{1cm} (1.25)

Now the matrix $G$ is defined as

$$G = DD^T$$  \hspace{1cm} (1.26)

The relation between $G$, $M$ and $B$ is

$$G = BM^{-1}B^T$$  \hspace{1cm} (1.27)

The kinetic energy in terms of velocities of internal coordinates is

$$2T = \dot{R}^T G^{-1} \dot{R}$$  \hspace{1cm} (1.28)

and potential energy

$$2V = R^T FR$$  \hspace{1cm} (1.29)

Having obtained the kinetic and potential energies in the required form as functions of internal coordinates, the secular determinant can be obtained as

$$\begin{vmatrix} GF - \lambda E \end{vmatrix} = 0$$  \hspace{1cm} (1.30)

where $E$ is the unit matrix. The final form of the expression yields the product of $GF$ first described by Wilson and this method is referred to as the Wilson’s FG matrix method [14,15].
1.14. Computer Programs for Solving the Secular Equation

After introducing necessary modifications in the program developed by Fuhrer et al. [16], was used for the calculation of the vibrational frequencies of the molecules. The necessary information that is needed for the calculation is an initial vibrational force field and the structural parameters of the molecule; these parameters may be either the bond lengths and bond angles or the Cartesian coordinates of the atoms with respect to an arbitrary chosen origin. The program is designed to consist of modules so that the output from one serves as a part of the input to the next. The calculated frequencies and the potential energy distributions are obtained as output. The options available in the program are extended to analyse the data and to modify the force field systematically to improve the fit with the experimental values.

1.15. Potential Energy Distribution

In the normal coordinate analysis, the potential energy distribution (PED) plays an important role to obtain a detailed understanding about the nature of the normal modes. The PED is expressed in terms of the percentage contribution of each force constant or the displacement coordinate or symmetry coordinate to the potential energy of each normal mode. The potential energy is expressed by the equation (1.20) as

\[ 2V = \sum \lambda_i Q_i^2 \]  

(1.31)

If the unit displacements of the normal coordinate \( Q_i \) are considered all other normal coordinate being at rest, then \( \lambda_1 \) is a measure of the potential energy. The normalization condition \( L^f L = \lambda \) gives the relations of the form,

\[ \lambda_1 = \sum_{jk} L_{ij} f_{jk} L_{kl} \]  

(1.32)

and after neglecting the cross terms,

\[ \lambda_1 = \sum_j f_{jj} L_{jj}^2 \]  

(1.33)

Hence, the normalised PED is expressed as

\[ V_{ji} = \frac{f_{jj} L_{jj}^2}{\lambda_1} \]  

(1.34)
where, $V_{jl}$ is the contribution of the $j^{th}$ symmetry coordinate to the potential energy of the vibration whose frequency is $\nu_l$.

### 1.16. Computational Chemistry

Computational chemistry normally complement the information obtained by chemical experiments, it can in some cases predict hitherto unobserved chemical phenomena. It is widely used in the design of new drugs and materials. The properties such as structure (i.e. the expected positions of the constituent atoms), absolute and relative (interaction) energies, electronic charge, dipoles and higher multipole moments, vibrational frequencies, reactivity or other spectroscopic quantities, and cross sections for collision with other particles can be evaluated [17,18]. Computational chemistry can assist the experimental chemist or it can challenge the experimental chemist to find entirely new chemical objects. To summarise, computational chemistry is:

- a branch of chemistry that generates data which complements experimental data on the structures, properties and reactions of substances. The calculations are based primarily on Schrodinger's equation and include
  - electronic structure determinations
  - geometry optimisations
  - frequency calculations
  - transition structures
  - protein calculations, i.e. docking
  - electron and charge distributions
  - potential energy surfaces (PES)
  - rate constants for chemical reactions (kinetics)
  - thermodynamic calculations– heat of reactions, energy of activation and

- particularly useful for
  - determination of properties that are inaccessible experimentally
  - interpretation of experimental data

Computational quantum chemistry is primarily concerned with the numerical computation of molecular electronic structures by *ab initio* and semi–empirical techniques. Scientists mainly use three different methods to make calculations:

- *ab initio*, (Latin for "from the beginning") a group of methods in which molecular structures can be calculated using nothing but the Schrödinger
equation, the values of the fundamental constants and the atomic numbers of the atoms present. The *ab initio* methods primarily revolve around the solution of the non–relativistic, time independent, Schrödinger wave equation\([19–21]\).

- Semi–empirical techniques use approximations from empirical (experimental) data to provide the input into the mathematical models.
- Molecular mechanics uses classical physics to explain and interpret the behavior of atoms and molecules

### 1.17. Methods

The total energy is determined by approximate solutions of the time–dependent Schrödinger equation, usually with no relativistic terms included, and by making use of the Born–Oppenheimer approximation, which allows for the separation of electronic and nuclear motions, thereby simplifying the Schrödinger equation. This leads to the evaluation of the total energy as a sum of the electronic energy at fixed nuclei positions and the repulsion energy of the nuclei \([22–24]\). The ways of determining the total energy to predict molecular structures are:

#### 1.17.1. *Ab initio* Methods

The programs used in computational chemistry are based on many different quantum–chemical methods that solve the molecular Schrödinger equation associated with the molecular Hamiltonian. Methods that do not include any empirical or semi–empirical parameters in their equations–being derived directly from theoretical principles, with no inclusion of experimental data–are called *ab initio* methods. This does not imply that the solution is an exact one; they are all approximate quantum mechanical calculations. It means that a particular approximation is rigorously defined on first principles (quantum theory) and then solved within an error margin that is qualitatively known beforehand.

The simplest type of *ab initio* electronic structure calculation is the Hartree–Fock (HF) scheme, an extension of molecular orbital theory, in which the correlated electron–electron repulsion is not specifically taken into account; only its average effect is included in the calculation. As the basis set size is increased, the energy and wave function tend towards a limit called the Hartree–Fock limit \([25–27]\).

The total molecular energy can be evaluated as a function of the molecular geometry; in other words, the potential energy surface. Such a surface can be used for
reaction dynamics. The stationary points of the surface lead to predictions of different isomers and the structures for conversion between isomers [28,29].

1.17.2. Density Functional Methods

Density functional theory (DFT) methods are often considered to be *ab initio* methods for determining the molecular electronic structure, even though many of the most common functionals use parameters derived from empirical data, or from more complex calculations. This means that they could also be called semi–empirical methods. In DFT, the total energy is expressed in terms of the total one–electron density rather than the wave function. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density [30–33]. DFT methods can be very accurate for little computational cost.

1.17.3. Semi–empirical and Empirical Methods

Semi–empirical quantum chemistry methods are based on the Hartree–Fock formalism, but make many approximations and obtain some parameters from empirical data. They are very important in computational chemistry for treating large molecules where the full Hartree–Fock method without the approximations is too expensive. The use of empirical parameters appears to allow some inclusion of correlation effects into the methods.

Semi–empirical methods follow what are often called empirical methods, where the two–electron part of the Hamiltonian is not explicitly included. For π – electron systems, this was the Hückel method proposed by Erich Hückel, and for all valence electron systems, the Extended Hückel method proposed by Roald Hoffmann [34–36].

1.17.4. Molecular Mechanics

In many cases, large molecular systems can be modeled successfully while avoiding quantum mechanical calculations entirely. Mechanics simulations, for example, use a single classical expression for the energy of a compound, for instance the harmonic oscillator. All constants appearing in the equations must be obtained beforehand from experimental data or *ab initio* calculations. These methods can be applied to proteins and other large biological molecules, and allow studies of the approach and interaction (docking) of potential drug molecules.
1.18. *Ab initio Theory*

The calculation of the vibrational properties within *ab initio* theory is based on total energy calculations of the electronic system as a function of certain atomic displacements [37–40]. Frequencies and displacement patterns of all phonon modes can be obtained by diagonalising the dynamical matrix

\[ D(\alpha k, \beta k') = \frac{1}{\sqrt{m_k m_{k'}}} \phi(\alpha k, \beta k') \]  

(1.35)

where, \( \alpha \) and \( \beta \) are coordinate indices, and \( k, k' \) denote atoms in the unit cell with masses \( m_k \). The force constant matrix (FCM) \( \phi(\alpha k, \beta k') \) is given by the normalised change of the component \( F_\alpha \) of the force acting on atom \( k \) when atom \( k' \) is displaced in direction \( \beta \). In principle, the dynamical matrix depends also on \( q \), i.e. on the relative phase of the displacements of neighbouring molecules. However, since the intermolecular interactions are very weak, we can neglect their influence on the intramolecular vibrations and restrict ourselves to the zone center modes (\( q=0 \)).

1.19. *Hartree–Fock Theory*

The original Hartree method expresses the total wavefunction of the system as a product of one–electron orbitals. In the Hartree–Fock method, the wavefunction is an antisymmetrised determinantal product of one electron orbitals (the "Slater" determinant). Schrödinger's equation is transformed into a set of Hartree–Fock equations. In Hartree–Fock (HF) theory the energy of a system is given as a sum of five components:

\[ E_{HF} = E_{NN} + E_T + E_v + E_{coul} + E_{exch} \]  

(1.36)

The nuclear–nuclear repulsion \( E_{NN} \) describes the electrostatic repulsion between the nuclei and is independent of the electron coordinates. In time–independent HF theory, the kinetic energy of the nuclei is not, but the kinetic energy of the electrons \( E_T \) is considered. Together with the nuclear–electron attraction energy \( E_v \) it depends on the coordinates of one electron. The classical electron–electron coulomb repulsion energy \( E_{coul} \) and the non–classical electron–electron exchange energy \( E_{exch} \) depend on the coordinates of two electrons. Calculation of these last two terms constitutes the main effort in HF calculations and is also responsible for the unfavorable formal scaling of computational effort as the fourth power of basis functions used for the description of the wavefunction. The particular assumption made in HF theory is that each electron
feels the other electrons only as an average charge cloud, but not as individual electrons.

The molecular electronic wavefunction in HF theory is based on the LCAO (Linear Combination of Atomic Orbitals) scheme describing each molecular orbital (holding one electron) as a linear combination of basis functions:

\[ \Phi_i = \sum C_{\mu i} \chi_{\mu} \]

where \( \Phi_i \) is molecular orbital \( i \), \( C_{\mu i} \) is molecular orbital coefficient and \( \chi_{\mu} \) is the basis function. The molecular orbital coefficients describe the contribution of each of the basis functions to a given molecular orbital. The overall electronic wavefunction of the system is constructed as an antisymmetrised product of the molecular orbitals (the Slater determinant) in order to fulfill the Pauli exclusion principle. Since the optimal shape of one molecular orbital depends on the shape of all the other occupied molecular orbitals, the optimisation of the overall wavefunction is achieved in an iterative manner, varying the molecular orbital coefficients until no further changes in the overall wavefunction occur. The direction of the variation of MO coefficients is guided by the variational principle stating that approximate wavefunction yields energy of the system which is higher than the energy obtained from the exact wavefunction. In other words, in order to arrive at most favorable wavefunction the MO coefficients must be varied such that the energy of the system becomes as low as possible.

1.20. The Hartree–Fock Equations

Having chosen Slater determinants as trial functions and having worked out the rules needed to evaluate the Average Value Theorem, the next step in a variational method is to minimize the expectation value of the Hamiltonian with respect to the variational parameters in the Slater determinant, the set of LCAO–MO coefficients in the spin orbitals, and thereby find the best single Slater determinant description of the molecular system. Collectively, this process is called the Hartree–Fock method [36,41,42]. From Slater's rules, the expectation value of the total energy for a molecule in the state given by the determinant |\( S \rangle \) is

\[ f = E_0 = \langle S | \hat{H} | S \rangle = \sum_{a} \langle a | \hat{H} | a \rangle + \frac{1}{2} \sum_{ab} \langle ab \parallel ab \rangle \]  

\[ (1.37) \]
In order to use Slater's rules, it is assumed that the set of spin orbitals are orthonormal and that they satisfy

\[ g = \langle a|b \rangle - \delta_{ab} = 0 \]  

(1.38)

This constraint, \( g \), together with the energy functional, \( f \), can be used to minimise \( f \) using the method of Lagrange's undetermined multipliers. In order to employ this method one combines the constraint and energy functionals by introducing a set of undetermined multipliers, denoted by \( \epsilon_{ab} \), with the foreknowledge that in the end they will represent orbital energies:

\[ L = f - \sum_{a}^{N} \sum_{b}^{N} (\epsilon_{ab} \langle a|b \rangle - \delta_{ab}) \]  

(1.39)

The next step in Lagrange's method of undetermined multipliers is to set the first variation of \( L \) to zero:

\[ \delta L = 0 = \delta f - \sum_{a}^{N} \sum_{b}^{N} E_{ab} \delta \langle a|b \rangle \]  

(1.40)

Upon expansion, followed by simplification in which \( a \) and \( b \) are replaced by the respective spin orbitals, \( \chi_a \) and \( \chi_b \), one eventually arrives at a sum of complex conjugates:

\[ \delta L = 0 \]

\[ = \sum_{a}^{N} \langle \delta \chi_a | \hat{h} | \chi_a \rangle + \sum_{a}^{N} \sum_{b}^{N} E_{ab} \delta \langle ab | ab \rangle - \langle ab | ba \rangle \]

\[ - \sum_{a}^{N} \sum_{b}^{N} E_{ab} \delta \langle a|b \rangle + \text{complex conjugate} \]  

(1.41)

At this juncture it is convenient to introduce two operators, the Coulomb and exchange operators, \( \hat{f} \) and \( \hat{R} \), which will help reduce the equations:

\[ \hat{f} = \int dx_2 |X_2(X_2)|^2 \frac{1}{r_{12}} \]  

(1.42)

\[ \hat{R} = \int dx_2 \chi_b^*(X_2) \frac{1}{r_{12}} \chi_b(X_2) \]  

(1.43)

These two particular operators are chosen because they have the following expectation values:

\[ \langle \chi_a | \hat{f} | \chi_b \rangle = \langle ab | ab \rangle \]  

(1.44)
and \( \langle \chi_a | \vec{R} | \chi_b \rangle = \langle ab | ba \rangle \) (1.45)

allowing the minimisation condition to be rewritten as

\[
\delta L = \sum_a^N \int dX_i \delta \chi_a(1) \left[ h(1)\chi_a(1) + \sum_b^N \left( \delta(1) - R_b(1) \right) \chi_a(1) - \sum_a^N E_{ab} \right]
+ \text{complex conjugate}
\]

Moreover, the quantity \( \delta \chi_a^*(1) \) is an arbitrary variation in \( \chi_a^*(1) \), and therefore, if the right side of the above equation is equal to zero for all possible cases, the quantity in brackets must also equal to zero:

\[
\left[ h(1)\chi_a(1) + \sum_b^N \left( \delta(1) - R_b(1) \right) \chi_a(1) - \sum_a^N E_{ab} \right] = 0
\]

(1.47)

Moving the term involving \( \chi_b \) to the other side of the equal sign yields

\[
\left[ h(1) + \sum_b^N \left( \delta(1) - R_b(1) \right) \right] \chi_a(1) = \sum_a^N E_{ab}
\]

(1.48)

The quantity in brackets on the left–hand side of the equal sign is known as the Fock operator, denoted by \( \hat{f} \). Thus, the minimisation condition is reduced to the convenient operator equation

\[
\hat{f} | \chi_a \rangle = \sum_b^N E_{ab} | \chi_b \rangle
\]

(1.49)

The minimisation condition given above is not in the standard or canonical form of eigen value equation. In quantum mechanics, when an operator acts upon a state function that is compatible with it, one fully expects to get an eigen value equation. In the case of the Fock operator, one can expect the Slater determinant and the Fock operator to be compatible given the method of their construction; hence, an eigen value equation should result. The minimisation criteria takes a non–canonical form because any single Slater determinant wave function \( | \Psi \rangle \) formed from a set of spin orbitals \( \chi_a \) retains a certain degree of flexibility in the spin orbitals: the spin orbitals can be mixed among themselves without changing the expectation value \( E_0 = \langle \Psi | h | \Psi \rangle \). Fortunately, it is possible to cast the above minimisation criterion into an eigen value equation by transforming the spin orbitals into a set of canonical spin orbitals through a unitary transformation of the general form.
where, \( U \) is a unitary matrix and \( U^\dagger \) is its inverse. The unitary matrix \( U \) is chosen such that the matrix of undetermined multipliers \( E \) with entries \( E_{ab} \) is diagonalised after the unitary transformation

\[
U E U^\dagger
\]

Upon completion of some mathematically allowable unitary transformation of the form described, the minimisation criterion is finally cast into the standard form known as the canonical Hartree–Fock equation:

\[
\hat{f} |\chi_a\rangle = E_a |\chi_a\rangle
\]

1.21. SCF Method

The SCF method provides a computationally tractable means of obtaining an approximate wave function and absolute total energy for a many electrons system. Many of the properties of interest can be found by constructing the full potential energy surface (PES) by performing an SCF calculation. By finding the minima on the PES, one can find stable nuclear configurations that could be observed in the laboratory and report spectroscopic information such as bond lengths, bond angles, and rotational constants to experimentalists. One can also find other stationary points on the PES which correspond to transition states for interconversion between minima and, thereby, provide experimentalists with reaction pathways and energy barriers. In order to reduce the computational effort and yet extract as much of the desired information as possible, quantum chemists use derivatives of the absolute energy [18]. From the gradient of the energy one can find stationary points such as minima and transition states by following paths of steepest ascent or descent. From the second derivative one can find the curvature of the PES around a stationary point and predict harmonic vibrational frequencies. From higher derivatives one can find higher order spectroscopic constants such as anharmonicity [43–45].

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

\[
\hat{\bar{\Omega}} = \sum_{i}^{N} \hat{\bar{\Omega}}_i
\]

and the expectation value of \( \hat{\bar{\Omega}} \) as given by Slater's rules is
\begin{equation}
\langle \Psi_0 | \hat{\mathcal{O}} | \Psi_0 \rangle = \sum_{\alpha}^{N/2} \langle \psi_\alpha | \hat{\mathcal{O}} | \psi_\alpha \rangle = \sum_{uv} P_{uv} (v|\mathcal{O}|u) \tag{1.54}
\end{equation}

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

\[ \mu = \sum_i q_i \mathbf{r}_i \tag{1.55} \]

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

\[ \mu = \langle \Psi_0 | - \sum_i \mathbf{r}_i | \Psi_0 \rangle = \sum_A Z_A R_A \tag{1.56} \]

where the contributions of the electrons and nuclei have been separated into the first and second sums, respectively. From equation (1.56), the electronic contribution can be rewritten in terms of the known atomic orbital basis and the density matrix producing

\[ \mu = - \sum_{uv} P_{uv} (v|\mathbf{r}|u) + \sum_A Z_A R_A \tag{1.57} \]

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

\[ \rho (\mathbf{r}) = \sum_{uv} P_{uv} \phi_u (\mathbf{r}) \phi_v^* (\mathbf{r}) \tag{1.58} \]

### 1.22. Density Functional Theory

Density functional theory is an extremely successful approach for the description of ground state properties of organic compounds, metals, semiconductors, and insulators. The success of density functional theory (DFT) not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes. The main idea of DFT is to describe an interacting system of fermions via its density and not via its many–body wave function. For \( N \) electrons in a solid, which
obey the Pauli principle and repulse each other via the Coulomb potential, this means that the basic variable of the system depends only on three; the spatial coordinates $x$, $y$, and $z$; rather than $3N$ degrees of freedom. While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on approximations for the so–called exchange–correlation potential. The exchange–correlation potential describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons.

A common approximation is the so–called local density approximation (LDA) which locally substitutes the exchange–correlation energy density of an inhomogeneous system by that of an electron gas evaluated at the local density. In density functional theory, the energy is not written in terms of the many–electron wave function as is conventional in quantum chemistry, but as a functional of the electron density. Kohn and Sham proposed that the functional for a system of electrons with external field $V_{\text{ext}}(x)$ be written in the form

$$E_{ks}[\rho(x)] = T_s[\rho(x)] + E_{ex}[\rho(x)] + E_{xc}[\rho(x)] + E_{ext}[\rho(x)]$$  \hspace{1cm} (1.59)$$

The ground state of a system of electrons in an external field (such as that due to a collection of nuclei) is given by minimizing the density functional, Eq. 1.59. The formal statement of the DFT is that the minimum of the functional corresponds to the ground state of the many–electron system. The practical way of solving the DFT problem is to introduce single–particle wavefunctions that give rise to the electron density $\rho(x)$ and to solve Kohn–Sham equations for them:

$$\left\{-\frac{\hbar^2}{2m} + V_{\text{eff}}(x) - \varepsilon_n\right\} \phi_n(x) = 0$$  \hspace{1cm} (1.60)$$

where effective potential includes Hartree, exchange–correlation and external potentials. An efficient way of solving Eq. 1.60 is to expand the wavefunctions using a convenient basis set and to minimise the DFT functional by varying expansion coefficients.

1.23. Hohenberg–Kohn Theorems

DFT was put on a firm theoretical footing by the Hohenberg–Kohn. The first of these demonstrates the existence of a one–to–one mapping between the state electron density and the ground state wavefunction of a many–particle system. Further, the second H–K theorem proves that the ground state density minimises the total electronic energy of the system. The original H–K theorems held only for the
ground state in the absence of magnetic field, although they have since been
generalised [46].

The first Hohenberg–Kohn theorem is an existence theorem; tell us that the
electron density that minimises the energy according to the true total energy
functional describes all that can be known about the electronic structure. The H–K
theorems do not tell us what the true total energy functional is, only that it exists.

The most common implementation of density functional theory is through the
Kohn–Sham method, which maps the properties of the system onto the properties of a
system containing non–interacting electrons under a different potential. The kinetic
energy functional of such a system of non–interacting electrons is known exactly. The
exchange–correlation part of the total energy functional remains unknown, and must
be approximated.

1.23.1. Description of the Theory

The main objective of density functional theory is to replace the many–body
electronic wavefunction with the density as the basic quantity. Whereas the many–
body wavefunction 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.

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. The simplest
approximation is the local–density approximation (LDA), which is based upon exact
exchange energy for a uniform electron gas, which can be obtained from the Thomas–
Fermi model, and from fits to the correlation energy for a uniform electron gas.

1.23.2. Derivation and Formalism

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 a wave function $ψ(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ satisfying the
many–electron Schrödinger equation
\[ H\Psi = [T + V + U]\Psi = \left[ \sum_i^N - \frac{\hbar^2}{2m} \nabla_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j) \right]\Psi = E\Psi \quad (1.61) \]

where, \( H \) – the electronic molecular Hamiltonian, \( N \) – the number of electrons and \( U \) – 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.

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

\[ n(\vec{r}) = N \int d^3r_2 \int d^3r_3 \ldots \int d^3r_N \Psi^*(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N) \quad (1.62) \]

Hohenberg and Kohn proved in 1964 that the relation expressed above can be reversed, i.e., \( n_0(\vec{r}) \) to a given ground state density it is in principle possible to calculate the corresponding ground state wavefunction \( \Psi_0(\vec{r}_1, \ldots, \vec{r}_N) \). In other words, \( \Psi_0 \) is a unique functional of \( n_0 \), i.e.

\[ \Psi_0 = \Psi_0[n_0] \quad (1.63) \]

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

\[ \langle O \rangle[n_0] = \langle \Psi_0 \rangle[n_0]|O|\Psi_0[n_0] \quad (1.64) \]

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

\[ E_0 = E_0[n_0] = \langle \Psi_0 \rangle[n_0]|T + V + U|\Psi_0[n_0], \quad (1.65) \]

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

\[ V[n] = \int V(\vec{r})n(\vec{r})d^3r \quad (1.66) \]

The functionals \( T[n] \) and \( U[n] \) are called universal functionals 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 minimise the functional

\[ E[n] = T[n] + U[n] + \int V(\vec{r})n(\vec{r})d^3r \quad (1.67) \]
with respect to $n(\vec{r})$, assuming one has got reliable expressions for $T[n]$ and $U[n]$. A successful minimisation of the energy functional will yield the ground state density $n_0$ and thus all other ground state observables.

The variational problem of minimising 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. Hereby, one uses the fact that the functional in the equation above can be written as a fictitious density functional of a non-interacting system

$$E_s[n] = \langle \Psi_s[n] | T_s + V_s | \Psi_s[n] \rangle \tag{1.68}$$

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

$$V_s = V + U + (T - T_s) \tag{1.69}$$

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

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right\} \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}), \tag{1.70}$$

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

$$n(\vec{r}) \equiv n_s(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2 \tag{1.71}$$

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

$$V_s = V + \int \frac{e^2 n_s(\vec{r})}{|\vec{r} - \vec{r}'|} d^3r' + V_{XC}[n_s(\vec{r})] \tag{1.72}$$

where the second term denotes the so-called 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 $\phi_i$, which in turn depend 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 $n(\vec{r})$, then calculates the corresponding $V_s$ and solves the Kohn–Sham equations for the $\phi_i$. From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached.
1.24. Approximations (Exchange–Correlation Functionals)

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. The most widely used approximation is the local–density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

$$E_{XC}[n] = \int \epsilon_{XC}(n) n(r) d^3r$$  \hspace{1cm} (1.73)

The local spin–density approximation (LSDA) is a straightforward generalization of the LDA to include electron spin:

$$E_{XC}[n_1, n_1] = \int \epsilon_{XC}(n_1, n_1) n(r) d^3r$$  \hspace{1cm} (1.74)

Highly accurate formulae for the exchange–correlation energy density $\epsilon_{XC}(n_1, n_1)$ have been constructed from quantum Monte Carlo simulations of a free electron model [47]. Generalized gradient approximations (GGA) are still local but also take into account the gradient of the density at the same coordinate:

$$E_{XC}[n_1, n_1] = \int \epsilon_{XC}(n_1, n_1, \nabla n_1, \nabla n_1) n(r) d^3r$$  \hspace{1cm} (1.75)

Using the latter (GGA) very good results for molecular geometries and ground state energies have been achieved. Difficulties in expressing the exchange part of the energy can be relieved by including a component of the exact exchange energy calculated from Hartree–Fock theory. Functionals of this type are known as hybrid functionals.

1.25. Z–Matrices

Z–matrices find the cartesian coordinates of each atom in a molecule. These coordinates are used to describe characteristics of their molecule. It is important to identify the correct molecular geometry because small changes in geometry cause large changes in the molecular energy. Z–Matrices – converts the bond angles, bond lengths, and dihedrals of each atom in relation to other atoms in the molecule, into cartesian coordinates. A dihedral angle is formed from four atoms, and helps to define the dimensionality of the molecule. The diagram below explains the task.
1.25.1. Building of Z–Matrix
When constructing a Z–matrix, one should follow these steps:

1. Draw the molecule.

2. Assign one atom to be #1.

3. From the first atom, assign all other atoms a sequential number. When assigning atoms, you must be careful to assign them in an order that is easy to use. This will become clearer as you experiment with different molecules.

4. Starting with atom #1, list the atoms you numbered, in order, down your paper, one right under the other.

5. Place the atom designated as #1 at the origin of your coordinate system. The first atom does not have any defining measurements since it is at the origin.

6. To identify the second atom, you must only define its bond length to the first atom. Use the reference charts given.

7. For the third atom, you must define a bond length to atom #1 and a bond angle between atom #3 and atoms #1 and #2. (Bond angles are the angles between three atoms.)

8. To identify atom #4 and all other atoms, you must include a bond length, bond angle and a dihedral angle. (Dihedral angles are the angles between an atom and the plane created by three other atoms.) This is done by using neighbouring atoms to the atom you are describing.

1.26. Basis Sets
A basis set is a collection of basis functions. For carbon, nitrogen, and oxygen compounds, a minimum basis set is composed of a 1s function for each hydrogen and 1s, 2s and three 2p functions for each of the second-row atoms. More extensive and flexible sets of basis functions are in wide use. These basis sets may have two or more components in the outer shell, which are called split-valence sets. Basis sets may
include $p$ functions on hydrogen and/or $d$ and $f$ functions on the other atoms. These are called \textit{polarization functions}. The basis sets may also include \textit{diffuse functions}, which extend farther from the nuclear center. Split-valence bases allow description of tighter or looser electron distributions on atoms in differing environments. Polarization permits changes in orbital shapes and shifts in the center of charge. Diffuse functions allow improved description of the outer reaches of the electron distribution.

Pople developed a system of abbreviations that indicates the composition of the basis sets used in \textit{ab initio} calculations. The series of digits that follows the designation 3G or 6G indicates the number of Gaussian functions used for each successive shell. The combination of Gaussian functions serves to improve the relationship between electron distribution and distance from the nucleus. Polarization functions incorporate additional orbitals, such as $p$ for hydrogen and $d$ and/or $f$ for second-row atoms. This permits changes in orbital shapes and separation of the centers of charge. The inclusion of $d$ and $f$ orbitals is indicated by the asterisk (*). One asterisk signifies $d$ orbitals on second-row elements; two asterisks means that $p$ orbitals on hydrogen are also included. If diffuse orbitals are used they are designated by a plus sign (+) designation of double plus (++) means that diffuse orbitals are present on both hydrogen and the second-row elements. For example 6–311+G** conveys the following information:

- 6 – Core basis functions are represented as a single STO–6G expression.
- 311 – The valence set is described by three sets of STO–NG functions; each set includes an $s$ orbital and three $p$ orbitals. In the 6–311+G* basis there are three such sets. One is composed of three Gaussians (STO–3G expression of one $s$–type and three $p$–type forms) and the other two are represented by a single Gaussian (STO–1G) representation of the $s$–$p$ manifold. The collection of components of the split-valence representation can be designated by a series of primes.
- (+) Implies STO–1G diffuse $s$-$p$ manifold is included in the basis set for each non-hydrogen atom and
- (++) Implies that diffuse functions are also included for the hydrogen atoms.
In all of these approaches, in addition to the choice of method, it is necessary to choose a basis set. This is a set of functions, usually centered on the different atoms in the molecule, which are used to expand the molecular orbitals with the LCAO ansatz. *Ab initio* methods need to define a level of theory (the method) and a basis set. Two general types of basis functions are in common use, Slater [48,49] and Gaussian [50–52] functions. Slater type orbitals (STOs) are of the general form

\[ r^L e^{-\gamma r}, \text{ where } r = \left[ X^2 + Y^2 + Z^2 \right]^{1/2} \]  

(1.76)

and are chosen because they correctly describe the electron density of a molecule, having the correct cusp behavior near the nucleus and the correct fall–off behavior far away from the nucleus. In equation (1.77) \( L \) corresponds to the angular momentum quantum number of the orbital and \( \gamma \) reflects the spatial extent of the orbital. In the majority of *ab initio* methods an STO is approximated by either a single Gaussian type orbital (GTO) or a linear combination of GTOs:

\[ \psi_{GTO} = X^a Y^b Z^c e^{-\alpha r^2} \]  

(1.77)

\[ \psi_{STO} = \sum_{r=1}^{n} \psi_{GTO_r} \, dV \]  

(1.78)

In the expression for the GTO, the orbital exponent \( \alpha \) defines the spatial extent of the orbital; whereas, the sum of the exponents \( a, b, \) and \( c \) represents the angular momentum. STOs are more exact, but take much longer to calculate than GTOs. By adding several GTOs one can get a good approximation of the STO. Basis sets are named in the form: STO–NG. This means that you are modeling a STO calculation, with "N" number of GTOs. Asterisks at the end would imply an extended basis set. In the most general sense, a basis set is a table of numbers which mathematically estimate where the electrons can be found [53–59]. The general expression for a basis function is given as:

\[ \text{Basis Function} = N e^{(-\alpha \cdot r)} \]

where, \( N \) = Normalisation constant; \( \alpha \) = Orbital exponent and \( r \) = Radius in angstroms. Other standard basis sets are 6–31G, 6–31G*, 6–31G**, 6–311G**, and 6–311++G** [60–67].

1.27. Polarisation

Further improvement of basis functions is achieved by adding \( d \)--orbitals to all heavy (non–hydrogen) atoms.
For typical organic compounds these are not used in bond formation, as are the $d$–orbitals of transition metals.

They are used to allow a shift of the center of an orbital away from the position of the nucleus. For example, a $p$–orbital on carbon can be polarised away from the nucleus by mixing into it a $d$–orbital of lower symmetry (below).

One obvious place where this can improve results is in the modeling of small rings; compounds of second–row elements also are more accurately described by the inclusion of polarisation.

![Figure 1.6. Polarisation of $p$–orbital by mixing with a $d$–function](image)

The presence of polarisation functions is indicated in the Pople notation by appending an asterisk to the set designator. Thus, 3–21G* implies the previously described split valence basis with polarisation added. Typically, six $d$–functions ($x^2$, $y^2$, $z^2$, $xy$, $xz$, and $yz$), equivalent to five $d$–orbitals and one $s$, are used. Most programs can also use five real $d$–orbitals. An alternative description of this kind of basis is DZP: double zeta, polarisation. A second asterisk, as in the 6–31G** basis set implies the addition of a set of $p$–orbitals to each hydrogen to provide for their polarisation. Another alternative to the asterisk for specifying polarisation functions is $(d)$, placed after the G [68–73].

**1.28. Diffuse Functions**

To provide more accurate descriptions of anions, or neutral molecules with unshared pairs, basis sets may be augmented with so–called diffuse functions.

These are intended to improve the basis set at large distances from the nuclei, thus better describing the barely bound electrons of anions.

Processes that involve changes in the number of unshared pairs, such as protonation, are better modeled if diffuse functions are included.
The augmentation takes the form of a single set of very diffuse (exponents from 0.1 to 0.01) \(s\) and \(p\) orbitals.

All \textit{ab initio} programs offer at least one set of diffuse functions.

Diffuse Gaussians are usually of \(s\) and \(p\) type, however sometimes diffuse polarization functions are also used. Diffuse functions are necessary for correct description of anions and weak bonds (e.g. hydrogen bonds) and are frequently used for calculations of properties (e.g. dipole moments, polarisabilities, etc.). For the Pople's basis sets the following notation is used: \(n\–ij+G\), or \(n\–ijk+G\) when 1 diffuse \(s\–type\) and \(p\–type\) gaussian with the same exponents are added to a standard basis set on heavy atoms. The \(n\–ij++G\), or \(n\–ijk++G\) are obtained by adding 1 diffuse \(s\–type\) and \(p\–type\) gaussian on heavy atoms and 1 diffuse \(s\–type\) gaussian on hydrogens. The use of doubly–diffuse basis sets is especially useful to work with hydrides [74–77].

1.29. Vibrational Scaling Factors

The difference between the computed and the experimental frequencies may be due to many different factors, such as anharmonicity, errors in the computed geometry, Fermi resonance, etc. Even solvent effects may lead to systematic differences between computed and observed frequencies. The introduction of scaling factors is capable of accounting for all these various effects. The values of the force constants and the frequencies are close among similar molecules and characteristic groups. Based on this assumption, two procedures are frequently used for an accurate scaling. One possible approach involves the rescaling of the force constant matrix. A simple example is the proposal of Pulay and Meyer [78–82] to multiply all diagonal stretching force constants by 0.9 and to multiply all diagonal bending force constants by 0.8. These procedures certainly improve the agreement between computed and experimental frequencies since the computed values are usually too high by 5–10%.

Introduction of scaling factors for the frequencies themselves is preferable to the more indirect approach of scaling the force constants [83,84]. First, the frequencies are physically observable and the force constants are not. Second, the definition of the force constant matrix is not unique because the number of matrix elements is usually much larger than the number of known frequencies. The scaling of the frequencies is in general only carried out with the use of a unique scale factor, which is common for the same level of computation [85].
The calculated frequencies of the compounds were directly scaled by two procedures: using an overall scale factor for the calculated level and using a scaling equation determined for the benzene ring modes at each level. Single overall scale factor for the calculated level describes the scaling of all the computed frequencies of the molecules at a specific level of theory, with a unique scale factor (or correction factor), which is common for all the molecules with the same level of calculation. These scale factors differ for the different levels of theory, and it is the procedure generally used in the literature to scale the calculated frequencies. Scott et al. [85] recommended the use of two scale factors, one for the high and medium spectral wavenumbers and the other for the low frequency modes. In HF in which the two scale factors are reasonably close to one another so that the use of a single scale factor does not introduce significant error.

A better accuracy is obtained if a specific scale factor is used for each mode and level of calculation, although it requires slightly more effort. The procedure for the calculation of specific scale factor for each mode is based on the assumption that the ratios between experimental and computed frequencies are fairly constant for each type of characteristic frequency. It is then possible to derive for a known experimental spectrum a correction factor for each characteristic frequency by taking the average of the ratios between the experimental and computed frequencies, \( \lambda = \frac{\nu(\text{Exp})}{\nu(\text{Cal})} \) and to use them for predicting or assigning unknown spectra. The introduction of different scale factors for distinct types of vibrational modes, instead of using a uniform correction factor for all the modes, removes the error that is systematic and associated with the same mode in related molecules and, therefore, remarkably improves the accuracy of the methods in predicting the frequencies, especially the semiempiricals.

The scaling equations procedure gives rise to a more noticeable improvement in the predicted frequencies, than when a single overall scale factor is used. The density functional frequencies appeared to be more reliable predictions than the MP2 frequencies, and they were obtained at significantly less cost. The LYP correlation functional was slightly better than P86 and PW91. The basis set has little influence on B3LYP method.

The vibrational frequencies produced by \textit{ab initio} programs are often multiplied by a scale factor (in the range of 0.8 to 1.0) to better match experimental vibrational frequencies [85,86]. This scaling compensates for two problems:
1) The electronic structure calculation is approximate. Usually less than a relativistic full configuration interaction is performed.

2) The potential energy surface is not harmonic. For bond stretches a better description of the potential energy surface is given by the Morse potential

\[
E(x) = D[1 - \exp\left(-\beta(X - x_0)\right)]^2
\]

illustrated in Figure 1.7. In this equation \(E\) is the potential energy, \(D, \beta, \text{ and } x_0\) are constants, and \(x\) is the interatomic distance. The programs that predict vibrational frequencies do so by calculating the second derivative of the potential energy surface with respect to the atomic coordinates. This provides the curvature at the bottom (minimum) of the well. For a harmonic potential \(E(x) = kx^2\) this is directly related to the vibrational energy level spacing. For a Morse potential (with the same second derivative at the minimum) the anharmonicity causes the vibrational energy levels to be more closely spaced as illustrated in the Figure 1.7.

![Figure 1.7. Morse potential energy surface](image)

Experimentally usually the fundamental (\(v=0\) to \(v=1\) energy) is measured. If enough vibrational levels are observed a harmonic frequency can be estimated with a formula such as

\[
G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 + \ldots
\]

where \(G(v)\) is the vibrational energy, \(v\) is the vibrational quantum number, \(\omega_e\) is the harmonic frequency, and \(\omega_e x_e\) and \(\omega_e y_e\) are anharmonic constants. For polyatomic molecules usually only the fundamental is experimentally observed.
The scaling factor \((c)\) and its relative uncertainty \((u_r)\) are obtained from the experimentally observed vibrational frequencies \((\nu_i)\), and the theoretical vibrational frequencies \((\omega_i)\) by using the following sums over the vibrational frequencies:

\[
\begin{align*}
  c &= \frac{\sum \nu_i \omega_i}{\sum \omega^2} \\
  u_r &= \sum \omega^2 (c - \frac{\nu_i}{\omega_i})^2
\end{align*}
\]  

(1.80)  
(1.81)

1.29.1. How much do the factors change with basis set?

The Figure 1.8 shows several scaling factors and their uncertainties [87]. Filled circles = HF, filled squares = MP2, open circles = BLYP, open squares = B3LYP. The scaling factors depend weakly on basis set. The uncertainties are about twice as large for the 3–21G basis set as for the other basis sets, all of which include polarization functions. This suggests that polarization functions are important for avoiding markedly poor predictions of vibrational frequencies. For larger basis sets the scaling factors and uncertainties have non–significant changes.

Figure 1.8. Scaling factors and uncertainties
References


