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Theoretical Vibrational Spectroscopy: A Review

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ABSTRACT

Spectroscopy is the study of the interaction between radiation and matter as a function of wavelength. Theoretical vibrational spectroscopy has been discussed in this paper. In this paper, various approximations for solving Schrödinger Equation have been discussed. Ab-initio methods and DFT methods, various basis set have been discussed in details.

Keywords: Vibrational spectroscopy; Quantum mechanics; Schrödinger equation; Møller-Plesset theory

INTRODUCTION

Spectroscopy is the study of the interaction between radiation and matter as a function of wavelength. Spectroscopic analytical methods are based on measuring the amount of radiation produced or absorbed by molecular or atomic species of interest. Spectroscopic techniques have provided the most widely tools for the elucidation of molecular structure as well as the quantitative and qualitative determination of both inorganic and organic compounds. Recently, spectroscopy has emerged as a major analytical tool for biomedical applications and has made significant progress in the field of clinical evaluation. It is widely used in the study of biological and pharmaceutical materials.

Vibrational spectroscopy has significant contributions towards the studies of structure and physico-chemical properties of molecular systems. Its wide applications are in the study of intra molecular forces, intermolecular forces or degree of association in condensed phases and in the determination of molecular symmetries. The great value of vibrational spectroscopy in the molecular structure elucidation analysis of molecular systems has been well established [1-3]. Other applications include the identification of functional groups or compound identification, determination of the strength of chemical bond and the calculation of thermo dynamical properties. The general objective of any theory with molecular structure is to explain physical and chemical properties of the molecules in terms of the fundamental physical laws governing the behavior of its constituents. Quantum mechanics has proved itself as successful and reliable theory to interpret molecular spectra and to understand molecular properties [4]. The applicability of the general principle of quantum mechanics is so strong that many physical and chemical problems are being solved on a high-power computer rather than in the laboratory [4-8]. The rapid increase in computing power and the capability of theoretical methods and software have led to significant increase in the utility of quantum chemical approaches over the past decade. Improvements in quantum chemical methods have led to increased application to explore spectroscopy and structure of biologically active materials [9,10]. Its rapid development is opening the path to the study of increasingly large and chemically complex systems and, at the same time, to the possibility to perform affordable and accurate calculations of structural, dynamical, and spectroscopic properties of biomolecules. All quantum mechanical model starts from the Schrödinger equation in which molecules are treated as collections of nuclei and electrons.

SCHRÖDINGER EQUATION

In Schrödinger model molecules are treated as collections of nuclei and electrons. Schrödinger equation, for the hydrogen atom may be solved exactly. The Schrödinger equation for a general system is

$$\hat{\mathrm{H}}\Psi\left(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2, \ldots.\vec{\mathrm{r}}_{\mathrm{N}}, \vec{\mathrm{R}}_1, \vec{\mathrm{R}}_2, \ldots, \vec{\mathrm{R}}_{\mathrm{M}}\right) = \mathrm{E}\Psi\left(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2, \ldots.\vec{\mathrm{r}}_{\mathrm{N}}, \vec{\mathrm{R}}_1, \vec{\mathrm{R}}_2, \ldots, \vec{\mathrm{R}}_{\mathrm{M}}\right) \quad (1)$$

Where $\Psi\left(\vec{r}_1, \vec{r}_2, \ldots.\vec{r}_N, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M\right)$ is the wave function for all of the nuclei and electrons, which is a function of the electron positions $\vec{r}$ and the nuclear positions $\vec{R}$, E is the energy associated with this wave function and $\hat{H}$ is the Hamiltonian operator (or more simply the Hamiltonian) for the system containing P electrons and Q nuclei, which is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{I=1}^{Q}\frac{1}{M_I}\nabla_I^2 - \sum_{i=1}^{P}\sum_{I=1}^{Q}\frac{Z_I e^2}{4\pi\varepsilon_0 r_{iI}} + \sum_{i=1}^{P}\sum_{j>1}^{Q}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{I=1}^{Q}\sum_{J>I}^{Q}\frac{Z_I Z_J}{4\pi\varepsilon_0 R_{IJ}} \quad (2)$$

In atomic units ($\left(\hbar = m_e = e = 4\pi\varepsilon_0 = 1\right)$ this is just,

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{I=1}^{Q}\frac{1}{M_I}\nabla_I^2 - \sum_{i=1}^{P}\sum_{I=1}^{Q}\frac{Z_I}{r_{iA}} + \sum_{i=1}^{P}\sum_{j>1}^{P}\frac{1}{r_{ij}} + \sum_{I=1}^{Q}\sum_{J>I}^{Q}\frac{Z_I Z_J}{R_{IJ}} \quad (3)$$

Here Z is the nuclear charge, I and J run over the Q nuclei, i and j run over the P electrons,
M_I = Mass of nucleus I/ Mass of and electron,
R_{IJ}=distance between nuclei I and J,
rij =the distance between electrons i and j
r_{iI} = the distance between electron i and nucleus I
In Equation (3) the first term describes the total kinetic energy of the P electrons, the second term describes the total Kinetic energy of Q nuclei, the third term represent the attractive potential energy between the electrons, the fourth term represents the repulsive potential for electron-electron interaction whereas last term represents the repulsive potential energy for nucleus- nucleus interactions.
The many-electron Schrödinger equation cannot be solved exactly and so a number of approximations are required to make the mathematics tractable.

Ab-initio Methods

Ab Initio is a Latin term which means “from the beginning”. A calculation which starts from the first principle is called “ab initio”. It relies on fundamental laws of nature without additional constraints. In Ab-initio methods computations are done on theoretical principles without experimental data. In this method various mathematical approximations are used.

Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is the first of several approximations used to simplify the solution of Schrodinger equation. According to this approximation [11], the nuclei move much slower than the electrons due to their masses therefore, electrons are considered to be moving in the field of fixed nuclei so that the nuclear kinetic energy is zero and their potential energy is merely a constant.

The total molecular wave function $\Psi(\vec{r}, \vec{R})$ is the function of position of electrons and nuclei as the mass of electron is very less in comparison to nuclei, electron move very rapidly in order to conserve the momentum, thus any change in the position of nuclei is instantaneously responded by electrons. Thus the nuclear variables can be separated from the electron variables,

$$\Psi\left(\vec{r}_1, \vec{r}_2, \ldots.\vec{r}_P, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_Q\right) = \chi\left(\vec{r}_1, \vec{r}_2, \ldots.\vec{r}_P\right)\, \phi(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_Q\right) \quad (4)$$

This separation of the total wave function into an electronic wave function $\chi(\vec{r})$ and a nuclear wave function $\phi(\vec{R})$ means that the positions of the nuclei can be fixed, leaving it only necessary to solve for the electronic part. This approximation was proposed by Born and Oppenheimer and is valid for the vast majority of molecules. Born and Oppenheimer approximation leads to an “electronic” Schrödinger equation,

$$\hat{H}_{el}\chi\left(\vec{r}_1, \vec{r}_2, \ldots.\vec{r}_P\right) = E_{el}\chi\left(\vec{r}_1, \vec{r}_2, \ldots.\vec{r}_P\right) \quad (5)$$

with

$$\widehat{H}_{el} = -\frac{1}{2}\sum_{i=1}^{P}\nabla_i^2 - \sum_{i=1}^{P}\sum_{A=1}^{Q}\frac{Z_I}{r_{iI}} + \sum_{i=1}^{P}\sum_{j>i}^{P}\frac{1}{r_{ij}} \tag{6}$$

The term in equation (3) the second term which describes total Kinetic energy of Q nuclei is zero in equation (6) due to very low velocity of nuclei, and the fifth term describing the repulsive potential energy for nucleus- nucleus interactions in equation (3) is a constant. Thus the total energy, E, of the system will be the sum electronic energy, Eel and potential energy for nucleus- nucleus interactions, E_{Nuc}, i.e.

$E=E_{el}+E_{Nuc}$ where $$E_{Nuc} = \sum_{I=1}^{Q}\sum_{J>I}^{Q}\frac{Z_I Z_J}{R_{IJ}} \tag{7}$$

Hartree-Fock Approximation

In order to solve the Schrödinger equation some more approximations are required. The most obvious approximation is that one can assume that electrons are moving independent of each other.

In equation (4) the wave function we have seen that $\chi(\vec{r}_1, \vec{r}_2, ... \vec{r}_P)$ depends on the positions of the electrons in the molecule. Hartree [12] further proposed the idea of separation of variables used by Born and Oppenheimer by assuming that the electronic wave function $\chi(\vec{r}_1, \vec{r}_2, ... \vec{r}_P)$ can be separated into the product of wave function of each electron,

$$\chi(\vec{r}_1, \vec{r}_2, ... \vec{r}_P) = \chi_1(\vec{r}_1)\chi_2(\vec{r}_2)......\chi_P(.\vec{r}_P) \tag{8}$$

Hartree taken further approximation by assuming electron–electron repulsion term of the Hamiltonian in Eq. (6) as an expression that describes the repulsion an electron feels from the average position of the other electrons as effective field V_i^{eff}. With this assumption, the wave function $\chi_i(\overrightarrow{r_i})$ for each electron satisfy the Hartree equations

$$\left(-\frac{1}{2}\sum_{i=1}^{P}\nabla_i^2 - \sum_{i=1}^{P}\sum_{I=1}^{Q}\frac{Z_I}{r_{iI}} + V_i^{eff}\right)\chi_i(\vec{r}_i) = E_i\chi_i(\vec{r}_i) \tag{9}$$

Equation (9) defines a set of equations, one for each electron. Solving for the set of functions $\chi_i(\overrightarrow{r_i})$ is nontrivial because V_i^{eff} it depends on all of the functions $\chi_i(\overrightarrow{r_i})$. An iterative scheme is needed to solve the Hartree equations. First, a set of functions $(\chi_1, \chi_2, ...\chi_P)$ is assumed. These are used to produce the set of effective potential operators V_i^{eff}, and the Hartree equations are solved to produce a set of improved functions $\chi_i(\overrightarrow{r_i})$. These new functions produce an updated effective potential, which in turn yields a new set of functions $\chi_i(\overrightarrow{r_i})$. This process is continued until the functions $\chi_i(\overrightarrow{r_i})$ no longer change, resulting in a self-consistent field (SCF).

Fock [13, 14] recognized that the separable wave function employed by Hartree (Eq. (8)) does not satisfy the Pauli Exclusion Principle [15] instead; Fock suggested using the Slater determinant [16]

$$\chi(\vec{r}_1, \vec{r}_2, ... \vec{r}_N) = \frac{1}{\sqrt{P!}}\begin{vmatrix} \chi_1(\vec{r}_1) & \chi_2(\vec{r}_1) & \cdots & \chi_P(\vec{r}_1) \\ \chi_1(\vec{r}_2) & \chi_2(\vec{r}_2) & \cdots & \chi_P(\vec{r}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\vec{r}_P) & \chi_2(\vec{r}_P) & \cdots & \chi_P(\vec{r}_P) \end{vmatrix} \tag{10}$$

This is antisymmetric and satisfies the Pauli Exclusion Principle. Again, an effective potential is employed, and an iterative scheme provides the solution to the Hartree–Fock (HF) equations.

Linear Combination of Atomic Orbitals (LCAO) approximation

The solutions to the Hartree-Fock model, χ_i, are known as the *molecular orbitals* (MOs). These orbitals generally span the entire molecule, just as the atomic orbitals (AOs) span the space about an atom.

The Hartree-Fock approximation leads to a set of Hartree-Fock equations (9) for each electron. In order to solve these equation numerically, an additional approximation LCAO has been introduced which transform the Hartree-Fock equations into a set of algebraic equations.

Since molecules are made up of atoms, thus molecular solutions can be expressed in terms of atomic solutions. In practice, the molecular orbitals are expressed as linear combinations of atomic orbitals

$$\chi_i = \sum_{\mu=1}^{k} C_{\mu i}\tilde{\phi}_{\mu} \tag{11}$$

Where the index μ spans all of the AOs $\tilde{\phi}_{\mu}$ of every atom in the molecule (a total of k AOs), $C_{\mu i}$ is the molecular orbital coefficient of AOs $\tilde{\phi}_{\mu}$ in MOs χ_i, for each spin orbital i. The basis functions $\tilde{\phi}_{\mu}$ are hydrogen-like atomic orbitals that have been optimized by a variational procedure. The HF procedure is a variational procedure to minimize the coefficients $C_{\mu i}$.

Hartree-Fock-Roothaan Procedure

Combining the LCAO approximation for the MOs with the HF method led Roothaan [20] to develop a procedure to obtain the self-consistent field (SCF) solutions. The procedure rests upon transforming the set of equations listed in Eq. (9) into matrix form

$$FC = \boldsymbol{\varepsilon} SC \tag{12}$$

Where, **S** is the overlap matrix (a measure of the extent to which basis functions “see each other”), **C** is the *k* × *k* matrix of the coefficients $C_{\mu i}$, and $\boldsymbol{\varepsilon}$ is the *k* × *k* matrix of the orbital energies. Each column of **C** is the expansion of χ_i in terms of the AOs $\tilde{\phi}_{\mu}$, **F** is the Fock matrix, which is analogous to the Hamiltonian in the Schrödinger equation. The Fock matrix **F** is defined for the $\mu\nu$ element as

$$F_{\mu\upsilon} = H_{\mu\upsilon}^{core} + J_{\mu\upsilon} - K_{\mu\upsilon} \tag{13}$$

$H_{\mu\upsilon}^{core}$ is the so-called core Hamiltonian, the elements of which are given by,

$$H_{\mu\upsilon}^{core} = \int \tilde{\phi}_{\upsilon}^{*}(\vec{r})\left[-\frac{1}{2}\nabla^{2} - \sum_{A=1}^{M}\frac{Z_A}{r_A}\right]\tilde{\phi}_{\upsilon}(\vec{r})\, d\vec{r} \tag{14}$$

Coulomb and exchange elements are given by,

$$J_{\mu\upsilon} = \sum_{\lambda=1}^{k}\sum_{\sigma=1}^{k} P_{\lambda\sigma}\left(\mu\upsilon \mid \lambda\sigma\right) \tag{15}$$

$$K_{\mu\upsilon} = \sum_{\lambda=1}^{k}\sum_{\sigma=1}^{k} \frac{1}{2} P_{\lambda\sigma}\left(\mu\lambda \mid \upsilon\sigma\right) \tag{16}$$

Where P is the density matrix whose elements involve a product of two molecular orbital coefficients as given below

$$P = 2 \sum_{i}^{\substack{occupied\\ molecular\\ orbitals}} c_{\lambda i}^{*}\ c_{\sigma i} \tag{17}$$

The electron density will be obtained by multiplying an element of the density matrix and its associated atomic orbitals and then summed over all orbitals.

(μν | λσ) are two-electron integrals and are given by

$$\left(\mu\upsilon \middle| \lambda\sigma\right) = \iint \tilde{\phi}_{\mu}^{*}(\vec{r}_1)\tilde{\phi}_{\upsilon}(\vec{r}_1)\left[\frac{1}{r_{12}}\right]\tilde{\phi}_{\lambda}^{*}(\vec{r}_2)\tilde{\phi}_{\sigma}(\vec{r}_2)\, d\vec{r}_1 d\vec{r}_2 \tag{18}$$

Because they are so numerous, the evaluation and processing of two electron integrals constitute the major time-consuming steps.

Since Hartree Fock matrix F depends on its own solution (through the orbitals), the process must be done iteratively. This is why the solution of the Hartree-Fock-Rothaan equations is often called the self-consistent-field (STF) procedure. In practice, a self-consistent method is used as follows:

i) Initial orbitals are chosen by using an approximate version of MO theory, e.g. some version of Hucket theory.
ii) Fock equations are solved to give an improved set of orbitals.
iii) These orbitals are compared to the previous set; If they are identical within some or numerical convergence threshold, it is stopped.
iv) Step 2 is repeated, using the improved orbitals as input.

With a reasonable set of "guess" orbitals to start off with, 10-20 cycles are usually enough to the procedure to numerical accuracy. For most of the calculations described, Hartree-Fock calculations are used to obtain vibrational frequencies, intensities and structural parameters of the molecules.

Methods resulting from solution of the Hartree-Fock-Rothaan equations are termed Hartree-Fock models. The corresponding energy is termed the Hartree-Fock energy.

The term *Ab initio* ("from the beginning") method is generally used for Hartree-Fock method but this should be all methods which rely on fundamental laws of nature without additional constraints in order to solve the Schrödinger equation.

Hartree-Fock models are both size consistent and variational. Hartree-Fock method can be used for molecules consisting of 50-100 atoms.

MØLLER-PLESSET THEORY

In Hartree-Fock models motion of each electron is assumed independent of the one another. Thus in the Hamiltonian interactions between individual electrons has been replaced by as an expression that describes the repulsion an electron feels from the average position of the other electrons as effective field. Due to this approximation the electron-electron repulsion energy become high and therefore total energy becomes too high

Møller-Plesset Perturbation Theory [18] is a widely used method for approximating the correlation energy (the difference between the Hartree-Fock energy and the experimental energy).of molecules. In particular, second order Møller-Plesset theory (MP2) probably the simplest useful wave function-based electron correlation method. Revived in the mid-1970s, it remains highly popular today, because it offers systematic improvement in optimized geometries and other molecular properties relative to Hartree-Fock (HF) theory. The MP3 method is still occasionally used, while MP4 calculations are quite commonly employed as part of the Gaussian 2 and Gaussian 3 thermo chemical methods. In the remainder of this section, the theoretical basis of Møller-Plesset theory is reviewed.

In Møller-Plesset models, second order Møller-Plesset theory (MP2) is the simplest member. In MP2 model it is assumed that Hartree Fock wave function Ψ_0 and ground state energy E_0 are exact solutions to an analogous problem involving the Hartree-Fock Hamiltonian, $\hat{H}_0$, in place of the "exact" Hamiltonian, $\hat{H}$. If we assume that Hartree-Fock wavefunction Ψ_0 and energy E_0 are very close to the exact wave function Ψ and ground-state energy E, then exact Hamiltonian can be written in the following form,

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \tag{19}$$

Here, $\hat{V}$ is a small perturbation and λ is a dimensionless parameter. Expanding the exact wave function and energy in terms of the Hartree- Fock wave function and energy yields.

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \dots\dots\dots \tag{20}$$

$$\Psi = \Psi_0 + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)} + \dots\dots\dots \tag{21}$$

Substituting the expansions (1-3) into the Schrödinger equation $\hat{H}\Psi = E\Psi$ and gathering terms in λ^n yields.

$$\hat{\mathrm{H}}_0 \Psi_0 = \mathrm{E}^{(0)} \Psi_0 \tag{22a}$$

$$\hat{H}_0 \Psi^{(1)} + \hat{V}\Psi_0 = E^{(0)} \Psi_1 + E^{(1)} \Psi_0 \tag{22b}$$

$$\hat{H}_0 \Psi^{(2)} + \hat{V}\Psi^{(1)} = E^{(0)} \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Psi_0 \tag{22c}$$

Multiplying each of the equations (22a-22c) by Ψ_0 and integrating over all space yields the following expression for the n^th^ order (MPn) energy.

$$E^{(0)} = \int \dots\dots \int \Psi_0^* \hat{H}_0 \Psi_0 \, d\tau_1 d\tau_2 \dots\dots\dots d\tau_n \tag{23}$$

$$E^{(1)} = \int \dots\dots \int \Psi_0^* \hat{V} \Psi_0 \, d\tau_1 d\tau_2 \dots\dots\dots d\tau_n \tag{24}$$

$$E^{(2)} = \int \dots\dots \int \Psi_0^* \hat{V} \Psi^{(1)} \, d\tau_1 d\tau_2 \dots\dots\dots d\tau_n \tag{25}$$

In this framework, the Hartree-Fock energy

$$E_0 = \int \dots\dots \int \Psi_0^* (\hat{H}_0 + \hat{V}) \Psi_0 \, d\tau_1 d\tau_2 \dots\dots\dots d\tau_n \tag{26}$$

Which is the sum of the zero and first-order Møller-Plesset energies,

$$E_0 = E^{(0)} + E^{(1)} \tag{27}$$

Therefore, we need to go beyond the first order energy in order to include correlation effect. The correlation energy can then be written

$$E_{corr} = E^{(2)} + E^{(3)} + E^{(4)} + \ldots\ldots \tag{28}$$

In which first term is MP2 energy.

It can be shown that the MP2 energy can be written (in terms of spin-orbitals) as

$$E^{(2)} = \sum_{i\langle j}^{occ}\sum_{a\langle b}^{unocc} \frac{[(ij \parallel ab)]^2}{(\varepsilon_a + \varepsilon_b + \varepsilon_i + \varepsilon_j)} \tag{29}$$

Where ε_i and ε_j are energies of occupied molecular orbitals, ε_a and ε_b are energies of unoccupied molecular orbitals, and integrals (ij || ab) over filled (i and j) and empty (a and b) molecular orbitals, account for changes in electron-electron interactions as a result of electron promotion,

(ij || ab) = (ia | jb) - (ib | ja) (30)

Where the integrals (ia | jb) involve molecular orbitals and not basis functions.

$$(ia|jb) = \iint \Psi_i^*(\vec{r}_1)\Psi_a(\vec{r}_1)\left[\frac{1}{r_{12}}\right]\Psi_j^*(\vec{r}_2)\Psi_b(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 \tag{31}$$

Which can be written in terms of the two-electron repulsion integrals

$$(ia|jb) = \sum_{\mu}\sum_{\upsilon}\sum_{\lambda}\sum_{\sigma} c_{\mu i}c_{\upsilon j}c_{\lambda a}c_{\sigma b}(\mu\nu \mid \lambda\sigma) \tag{32}$$

Møller-Plesset theory terminated to second-order, or MP2, shows improvement over Hartree-Fock theory. MP2 is size consistent but it is not variational where as Hartree-Fock theory both size consistent and variational. But MP2 theory is useful for molecules of moderate size.

Higher-order Møller-Plesset models (MP3, MP4, etc.) have been formulated, but these are used to very small systems. In these higher-orders Møller-Plesset models geometry optimization needs to be done numerically because analytical derivatives are not available easily.

Also localized MP2 procedures (“LMP2”) have been developed. In which Hartree-Fock orbitals first localized then used in the MP2 procedure. For sufficiently large molecules, LMP2 reduces the number of integrals (ij || ab) which leads to reduction in computational effort, memory and disk requirements. Presently Localized MP3 and MP4 models are not available. But in future it may become available which will further reduce the computational effort, memory and disk requirements.

BASIS FUNCTIONS AND BASIS SETS

In order to solve for the energy and wavefunction within the Hartree–Fock– Roothaan procedure, the AOs must be specified. If the set of AOs is infinite, then the variational principle tells us that we will obtain the lowest possible energy within the HF–SCF method. This is called the *HF limit*, E_{HF}. This is *not* the actual energy of the molecule; recall that the HF method neglects instantaneous electron–electron interactions, otherwise known as *electron correlation*. Since an infinite set of AOs is impractical, a choice must be made on how to truncate the expansion. This choice of AOs defines the *basis set*. As we have seen that molecular orbitals are expressed as linear combinations atomic orbitals by the relation

$$\chi_i = \sum_{\mu=1}^{k} C_{\mu i}\tilde{\phi}_\mu \tag{33}$$

Where the index μ spans all of the AOs $\tilde{\phi}_\mu$ of every atom in the molecule (a total of k AOs), $C_{\mu i}$ is the molecular orbital coefficient of AOs $\tilde{\phi}_\mu$ in MOs χ_i. For each spin orbital i the basis functions $\tilde{\phi}_\mu$ are hydrogen-like atomic orbitals that have been optimized by a variational procedure.

Atomic Orbitals (AO) are the solutions of the Hartree-Fock equations for the atom, i.e. Atomic Orbital is wave function for a single electron in the atom. Now the term atomic orbital is known as “basis function”.

In the beginning the Slater Type Orbitals (STOs) were used as basis functions because for hydrogen atom these are similar to atomic orbitals. STOs are described in terms of the spherical coordinates as below:

$$\Phi_i(\varsigma, n, l, m; r, \theta, \phi) = Nr^{n-1}e^{-\zeta r}Y_{lm}(\theta, \phi) \tag{34}$$

Where N is normalization constant, ζ (zeta) is called orbital exponent, it controls the width of the orbital (large ζ gives tight function, small ζ gives diffuse function). The r, θ and ϕ are spherical coordinates, Y_{lm} is the angular momentum part (function describing the shape). The n, l, and m are principal, angular momentum, and magnetic quantum numbers, respectively. In STO the exponential term has a more important role to play. The exponential dependence on the distance between the nucleus and the electron mirrors the exact orbitals for the hydrogen atom. The exponential dependence ensures a fairy rapid convergence with increasing number of functions. STOs are primarily used for atomic and diatomic systems and in semi-empirical methods.

The Gaussian Type Orbitals (GTOs) (called also Cartesian Gaussian type orbitals) are expressed as:

$$\Phi(\alpha, l, m, n; x, y, z) = N\, x^l y^m z^n e^{-\alpha r^2} \tag{35}$$

Where N is normalization constant α is called exponent. The l, m and n are not quantum numbers but simply integral exponents and $r^2=x^2+y^2+z^2$.

The trade-off is that GTOs do differ in shape from the STOs, particularly at the nucleus where the STO has a cusp while the GTO is continually differentiable.

STO's are more accurate, but it takes longer to compute integrals using them therefore a linear combination of enough GTO's to mimic an STO. A combination of n Gaussians to mimic an STO is often called an "STO-nG" basis, even though it is made of Contracted Gaussian Type Orbitals (CGTOs)..

$$\Phi_{lmn}^{CGTO} = N \sum_i c_i x^l y^m z^n e^{-\alpha r^2} \tag{36}$$

Therefore, multiple GTOs are necessary to adequately mimic each STO, increasing the computational size. Basis sets comprising GTOs are the ones that are most commonly used. There are two general categories of basis sets:

Minimal Basis Set: A basis set that describes only the most basic aspects of the orbitals. All basis set equations in the form STO-nG (where n represents the number of GTOs combined to approximate the STO) are considered to be "minimal" basis sets e.g. STO-2G, STO-3G, STO-6G etc.

Extended Basis Set: A basis set with a much more detailed description. The "extended" basis sets, then, are the ones that consider the higher orbitals of the molecule and account for size and shape of molecular charge distributions. There are several types of extended basis sets: Double-Zeta, Triple- Zeta, Quadruple- Zeta Basis Sets ; plit-Valence Basis Sets; Polarized Basis Sets; Diffuse Basis Sets etc.

Double-Zeta, Triple-Zeta, Quadruple-Zeta Basis Sets

In the minimal basis sets, we assume that all orbitals are of the same shape. But it is not true. The double-zeta basis set allows us to treat each orbital separately in order to use the Hartree-Fock calculation. In double-zeta basis set, each atomic orbital is expressed as the sum of two Slater-Type Orbitals (STOs). Both orbitals are the same except for the value of ζ (zeta). The zeta depends on the largeness the orbital is. Both STOs are then added using some proportion. The size of the atomic orbital comes between the values of either of the two STOs. Similarly the triple and quadruple-zeta basis sets work, except we use three STOs in triple-zeta basis set and four STOs in quadruple-zeta basis sets instead of two STOs.

Split-Valence Basis Sets

Since most of chemistry focuses on the action of the valence electron Pople [19, 20] developed the split-valance basis sets, single zeta (SZ) in the core and double zeta (DZ) in the valance region.

In order to calculate double-zeta for every orbital takes too much effort. Many Scientists assumed that inner shell electrons are not of much use and simplified it by calculating a double- zeta basis set only for the valence orbital. This method is called a split-valence basis set e.g. 3-21G, 4-31G, and 6-31G etc.

3-21G is the simplest split valence basis set. 3-21G (in the Pople notation) means that the core orbitals are represented by three Gaussians, whereas the inner valence orbitals are represented by two Gaussian and outer valence orbital consists of one Gaussians.

Polarized Basis Sets

Even large multizeta basis sets will not provide sufficient mathematical flexibility to adequately describe the electron distribution in molecules. An example of this deficiency is the inability to describe bent bonds of small rings. Extending the basis set by including a set of functions that mimic the AOs with angular momentum one greater than in the valence space greatly improves the basis flexibility. These added basis functions are called polarization functions.

For carbon, adding polarization functions means adding a set of d GTOs while for hydrogen, polarization functions are a set of p functions. The designation of a polarized basis set is varied. One convention indicates the addition of polarization functions with the label "+P"; DZ+P indicates a DZ basis set with one set of polarization functions.

For the split-valence sets, addition of a set of polarization functions to all atoms but not hydrogen is designated by an asterisk, that is, 6-31G(d), and adding the set of p functions to hydrogen as well is indicated by double asterisks, that is, 6-31G(d,p). Since adding multiple sets of polarization functions has become broadly implemented, the use of asterisks has been deprecated in favor of explicit indication of the number of polarization functions within parentheses, that is, 6-311G(2df,2p) means that two sets of d functions and a set of f functions are added to non hydrogen atoms and two sets of p Functions are added to the hydrogen atoms.

Diffuse Basis Sets

For anions or molecules with many adjacent lone pairs, the basis set must be augmented with diffuse functions to allow the electron density to expand into a larger volume. For split-valence basis sets, this is designated by "+," as in 6-31+G(d). The diffuse functions added are a full set of additional functions of the same type as are present in the valence space. One '+' means that the 'p' orbitals are taken into consideration, while '++' signals that both 'p' and 's' orbitals are taken into consideration.

The Correlation-Consistent Basis Set

The split-valence basis sets developed by Pople, though widely used, have additional limitations made for computational expediency that compromise the flexibility of the basis set. The correlation-consistent basis sets developed by Dunning [21-23] are popular alternatives.

The split-valence basis sets were constructed by minimizing the energy of the atom at the HF level with respect to the contraction coefficients and exponents. The correlation-consistent basis sets were constructed to extract the maximum electron correlation energy for each atom.

The correlation-consistent basis sets are designated as "cc-pV*N*Z," to be read as correlation-consistent polarized split-valence *N*-zeta, where *N* designates the degree to which the valence space is split. As *N* increases, the number of polarization functions also increases. So, for example, the cc-pVDZ basis set for carbon is DZ in the valence space and includes a single set of d functions, and the cc-pVTZ basis set is TZ in the valence space and has two sets of d functions and a set of f functions. The addition of diffuse functions to the correlation-consistent basis sets is designated with the prefix *aug*-, as in aug-cc-pVDZ.

Density Functional Theory

Ab-initio methods in electronic structure theory are based on the many-electron wave function. Density functional theory (DFT) [8] is a quantum mechanical method which is useful for finding the electronic structure of many-body systems. In density functional theory many-body electronic wave function is replaced by electronic density. The electronic wavefunction is dependent on 3*n* variables: the *x*, *y*, and *z* coordinate of each electron. As such, it is quite complicated and difficult to readily interpret. The total electron density $\rho(\vec{r})$ is dependent on just three variables: the *x*, *y*, and *z* positions in space. Since $\rho(\vec{r})$is simpler than the wavefunction and is also observable, perhaps it might offer a more direct way to obtain the molecular energy.

The Hohenberg–Kohn [24] existence theorem proves just that: there exists a unique functional such that

$$E[\rho(\bar{\mathrm{r}})] = E_{elec} \tag{37}$$

Where E_{elec} is the exact electronic energy. Furthermore, they demonstrated that the electron density obeys the variational theorem. This means that given a specific electron density, its energy will be greater than or equal to the exact energy. These two theorems constitute the basis of density functional theory (DFT). A mathematical *function* is one that relates a scalar quantity to another scalar quantity, that is, $y=f(x)$. A mathematical *functional* relates a function to a scalar quantity and is denoted within brackets, that is, $y=F[f(x)]$. In Eq. (37), the function $\rho(\vec{r})$depends on the spatial coordinates, and the energy depends on the values (is a functional) of $\rho(\vec{r})$. According to Hohenberg and Kohn (H-K) theorem, the total ground state energy and other properties of a system were uniquely defined by the electron density (the energy is a unique function of $\rho(\vec{r})$) and the true ground state electron density minimizes the energy functional. The H-K theorem gives proof of existence of such functional but there is no prescription to construct it. If it is known accurately, quantum chemical technique will be able to derive the molecular properties exactly. Till now the exact form of energy functional is not known. It is necessary to use approximations regarding various parts of the functional which deals the kinetic energy, exchange and correlation energies of the system of electrons. The simplest approximation is the Local-density approximation (LDA), The simplest approximation is the local density approximation (LDA) which leads to a Thomas-Fermi [25,26] term for kinetic energy and the Dirac [27] (actually Block proposed first [28]) term for the exchange energy. The corresponding functional is called Thomas-Fermi- Dirac energy. The Thomas-Fermi- Dirac with improvements is the present density functional method, since all components of energy are expressed via density alone without using many particle wave functions. However, wave functions cannot be completely neglected in molecular calculations and for accurate calculations they have to be used as a mapping step between the energy and density. So for a similar computational cost as the HF method, DFT produces the energy of a molecule that *includes the electron correlation.* This is the distinct advantage of DFT over the traditional *ab initio* methods discussed previously-it is much more computationally efficient in providing the correlation energy. HF and the various post-HF electron correlation methods provide an *exact* solution to an *approximate* theory, while DFT provides an *exact* theory with an *approximate* solution.

The Electron Density

The electron density is the central quantity in Density Functional Theory (DFT). It is defined as the integral over the spin coordinates of all electrons and over all but one of the spatial variables $(\vec{x} \equiv \vec{r}, s)$

$$\rho(\vec{r}) = N\int \dots \int |\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N \qquad (38)$$

$\rho(\vec{r})$ the probability of finding any of the N electrons within volume element $d\vec{r}$. Also $\rho(\vec{r})$ is a non-negative function of only the three spatial variables which vanishes at infinity and integrates to the total number of electrons, i.e.,

$$\rho(\vec{r} \to \infty) = 0 \text{ and } \int \rho(\vec{r}) d\vec{r} = N$$

The electron density is an observable and can be measured experimentally, e.g. by X-ray diffraction.

The Thomas-Fermi Model

The Thomas-Fermi model [25, 26] is based on the uniform electron gas, they proposed the following functional for the kinetic energy

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r})\, d\vec{r} \qquad (39)$$

The energy of an atom is finally obtained using the classical expression for the nuclear-nuclear potential and the electron-electron potential:

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r})\, d\vec{r} - Z\int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2}\int\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \qquad (40)$$

Which gives the energy is given completely in terms of the electron density. In order to determine the correct density to be included in Eq. (40), they employed a variational principle. They assumed that the ground state of the system is connected to the $\rho(\vec{r})$ for which the energy is minimized under the constraint of $\int \rho(\vec{r}) d\vec{r} = N$.

The First Hohenberg-Kohn Theorem

The first Hohenberg-Kohn [24] theorem demonstrates that the all the properties of the system can be determines by the electron density because electron density uniquely determines the Hamiltonian operator.

The first theorem states that the external potential $V_{ext}(\vec{r})$ is a unique functional of $\rho(\vec{r})$; because, $V_{ext}(\vec{r})$ fixes $\hat{H}$.

Thus the total ground state energy is a functional of density $\rho(\vec{r})$ which is the sum of three terms-the kinetic energy, the interaction with the external potential and electron-electron interaction and so we may write the functional as

$$\begin{aligned} E[\rho] &= T[\rho] + V_{ext}[\rho] + V_{ee}[\rho] \\ &= V_{ext}[\rho] + F_{HK}[\rho] \end{aligned} \qquad (41)$$

where $F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$ and $\mathrm{V_{ext}}(\rho) = \int \hat{\mathrm{V}}_{\mathrm{ext}} \rho(\vec{\mathrm{r}})\, \mathrm{d}\vec{\mathrm{r}}$.

The functional F_{HK} is unknown. The F_{HK} functional operates only on density and is universal, i.e., its form does not depend on the particular system under consideration. Also $V_{ee}[\rho]$ can be written as the sum of classical part $V_{cl}(\rho) = \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1\, d\vec{r}_2$ and non-classical part $V_{ncl}(\rho)$, thus

$$V_{ee}(\rho) = V_{cl}(\rho) + V_{ncl}(\rho)$$

i.e.

$$V_{ee}(\rho) = \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1\, d\vec{r}_2 + V_{ncl}(\rho) \tag{41a}$$

$V_{ncl}(\rho)$ is the non-classical contribution to the electron-electron interaction which includes self-interaction correction, exchange and coulomb correlation.

The Second Honberg-Kohn Theorem

The second Honberg-Kohn theorem states "$F_{HK}[\rho]$, the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density."

This is nothing but the variational principle:

$$E_0 \le E[\tilde{\rho}] = T[\tilde{\rho}] + V_{ext}[\tilde{\rho}] + V_{ee}[\tilde{\rho}] \tag{42}$$

In other words, this means that for any trial density $\tilde{\rho}(\vec{r})$, which satisfies the necessary boundary conditions such as

$$\tilde{\rho}(\vec{r}) \ge 0, \int \tilde{\rho}(\vec{r}) d\vec{r} = N \tag{43}$$

The energy obtained from the functional of $F_{HK}[\rho]$ represents an upper value to the true ground state energy E_0.

This theorem is useful for the study of the ground state. Hence, this strategy is not useful for the problems of excited states.

Both Honberg-Kohn theorems provide a fundamental statement of density functional theory;

$$\delta\left[E[\rho] - \mu\left(\int \rho(\vec{r})\, d\,\vec{r} - N\right)\right] = 0 \tag{44}$$

Where the multiplier of this constraint is the electronic *chemical potential* μ.

The Kohn-Sham Equations

The total ground state energy is a functional of density which contains three terms-the kinetic energy, the interaction with the external potential and electron-electron interaction and so we may write the functional as in Eq [41]

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho] \tag{45}$$

$$V_{ext}(\rho) = \int \hat{V}_{ext}\rho(\vec{r})\, d\vec{r}\,.$$

Kohn and Sham [29] proposed the following approach to approximating the kinetic and electron-electron functional. They introduced a fictitious system of N non interacting electrons to be described by a single determinant wave function in N "orbitals" ϕ_i. In this system the kinetic energy and electron density are known exactly from the orbitals;

$$T_s[\rho] = -\frac{1}{2}\sum_i^N \left\langle \phi_i \middle| \nabla^2 \middle| \phi_i \right\rangle \tag{46}$$

Here the suffix emphasises that this is not the true kinetic energy but is that of a system of non-interacting electrons, which reproduce the true ground state density;

$$\rho(\vec{r}) = \sum_i^N |\phi_i|^2 \tag{47}$$

Thus density can be constructed explicitly from a set of orbitals which ensures that density can be constructed from an asymmetric wavefunction.

Also the electron-electron interaction in the classical Coulomb interaction or Hartree energy (written in terms of the density) is written as;

$$V_H[\rho] = \frac{1}{2}\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{\vec{r}_{12}} d\vec{r}_1 d\vec{r}_2 \tag{48}$$

the energy functional given by Eq. [41] can be rearranged as;

$$\mathrm{E}[\rho] = \mathrm{T_s}[\rho] + \mathrm{V_{ext}}[\rho] + \mathrm{V_H}[\rho] + \mathrm{E_{XC}}[\rho] \tag{49}$$

where *exchange-correlation functional* has introduced [30]

$$\mathrm{E_{XC}}[\rho] = (\mathrm{T}[\rho] - \mathrm{T_s}[\rho]) + (\mathrm{V_{ee}}[\rho] - \mathrm{V_H}[\rho]) \tag{49a}$$

The *exchange correlation energy* $\mathrm{E_{XC}}$ is the functional that contains all the unknowns. It is the sum two terms (i) the error due to using a interaction between kinetic energies and (ii) the error due to assuming the electron-electron interaction classically. If we write the functional in terms of the density due to non-interacting orbitals and apply the variational theorem we find the following set of equations known as Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(r) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\,\vec{r}' + V_{xc}(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \tag{50}$$

In above equation a potential has been introduced which is the derivative of the exchange correlation energy with respect to the density,

$$\mathrm{v_{xc}(r)} = \frac{\delta \mathrm{E_{XC}}[\rho]}{\delta\rho} \tag{51}$$

This set of non-linear equations (the Kohn-Sham equations) describes the behaviour of non-interacting "electrons" in an effective local potential. For the exact functional, and thus exact local potential, the "orbitals" yield the exact ground state density via Equation [47] and exact ground state energy via Equation [49].

Walter Kohn was awarded with the Nobel Prize in Chemistry in 1998 for his development of the density functional theory.

The Local Density Approximation (LDA)

By applying various approximations for exchange correlation energy E_{xc} lead to a rapidly expanding field of research. The early assumption that leads to practical implementations of density functional theory was the homogeneous electron gas. In this system one assume that the electrons are subject to a constant external potential and therefore the charge density is constant. Such system is specified by the value of the constant electron density ρ=N/V.

Thomas and Fermi studied the homogeneous electron gas model [25, 26] by approximating the electron-electron interaction to the classical Hartree potential (neglecting the exchange and correlation effects) and computed the total energy functional. Under these assumptions the dependence of the kinetic and exchange energy on the density of the electron gas can be extracted (Dirac [27, 8, 31]) and expressed in terms of a *local* functions of the density.

Thus in the inhomogeneous system we might approximate the *functional* as an integral over a local *function* of the charge density. i.e.;

$$T[\rho] = 2.87\int \rho^{5/3}(\vec{r})\,d\vec{r}$$

and

$$E_X[\rho)] = 0.74\int \rho^{4/3}(\vec{r})\,d\vec{r}$$

These results are highly suggestive of a representation for E_{xc} in an inhomogeneous system. The local exchange correlation energy for each electron might be assumed as a function of the local charge density. This results in approximation of the form;

$$E_{XC}[\rho)] \approx \int \rho(\vec{r})\varepsilon_{XC}(\rho(\vec{r}))\,d\vec{r} \tag{52}$$

where $\varepsilon_{XC}(\rho(\vec{r}))$ to be the exchange and correlation energy density of the uniform electron gas of density $\rho(\vec{r})$ this is known as the **local density approximation (LDA)**. In **local density approximation** $\varepsilon_{XC}(\rho(\vec{r}))$ is a *function* of the local value of the density. $\varepsilon_{XC}(\rho(\vec{r}))$ can be separated into exchange and correlation energy;

$$\varepsilon_{XC}(\rho(\vec{r})) = \varepsilon_X(\rho(\vec{r})) + \varepsilon_C(\rho(\vec{r})) \tag{53}$$

The Dirac form can be used for $\varepsilon_X(\rho(\vec{r}))$

$$\varepsilon_X(\rho(\vec{r})) = -C\rho^{1/3}(\vec{r}) \tag{54}$$

Where a free constant, C, has been introduced. The functional form for the correlation energy density, ε_C, is unknown. In order to calculate for the homogeneous electron gas Monte Carlo calculations which yield essentially exact results [32]. The resultant exchange correlation energy has been used in a number of forms [33-35]. All the forms yield similar results and are collectively referred to as LDA functionals. The LDA is a fruitful approximation. Using LDA structure, vibrational frequencies, elastic moduli and phase stability (of similar structures) properties are described reliably for many systems.

The Generalized Gradient Approximation (GGA)

The local density approximation is considered to be the zeroth order approximation to the semi-classical expansion of the density matrix in terms of the density and its derivatives [36]. Beyond the LDA we use the gradient expansion approximation (GEA) in which in order to account for the non-homogeneity of the true electron density the first order gradient terms $\vec{\nabla}\rho(\vec{r})$ are included, Thus, the exchange-correlation energy can be written in following form which is termed generalized gradient approximation (GGA),

$$E_{XC} \approx \int \rho(\vec{r})\varepsilon_{XC}(\rho(\vec{r}),\vec{\nabla}\rho(\vec{r}))\,d\vec{r} \tag{55}$$

The GGA improves the LDA's description of the binding energy of molecules. A number of functionals in the GGA family [37-44] have been developed. Beck's 1988 exchange functional [45,46] in combination with the Perdew Wang 91 gradient-corrected correlation functional (BPW91) [47] and Beck's three parameter hybrid exchange functional using the Lee, yang and Parr functional (B3LYP)[48] were usually employed in the recent DFT calculation for bio-molecules.

Time Dependent Density Functional Theory

Over the last 35 years, density functional theory (DFT) has now become one of the standard methods for calculations in several branches of physics and chemistry. Systematic comparison of the results from DFT theory and experiments has shown [49,50] that the methods using Beck's theory parameter hybrid functional (B3) with correlation functions such as one proposed by Lee, Yang and Parr (LYP) is the most promising in providing the correct vibrational wave numbers.

In its original form, DFT is applicable only to ground states. One of the DFT approaches based on time-dependent density functional theory (TDDFT) have involved in recent times to deal with the excited state properties [51-53]. For calculation of transition energies and intensities, the TDDFT approach performs well. The results obtained using TDDFT are quite good for valence transitions [54-56]. The derivation for the time-dependent KS equations was first formulated in 1984 by Runge and Gross [57].

Scaling Procedures for HF and DFT Methods

Computational chemistry has become an important tool to aid in molecular identification by vibrational spectroscopy. Calculation of vibrational frequencies by *ab-initio* molecular orbital (MO) or density functional methods can help in the interpretation of experimental spectra and is particularly useful for reliable assignments of fundamental vibrational frequencies.

Unfortunately calculated vibrational frequencies usually overestimate the experimental fundamentals. This overestimation is due to three factors:

1. The overall neglect of anharmonicity,
2. An incomplete description of electron correlation due to the use of an incomplete basis set, and
3. An approximate method used to solve the Schrödinger equation.

The second factor arises because the computational cost for methods including electron correlation increases rapidly as the number of basis functions increases, preventing an advanced theoretical treatment for all but the very smallest of molecules [58].

The calculated vibrational frequencies need to be scaled down to bring them in accordance with the experimental results. Scaling factor has remained a point of debate with many quantum chemical calculations. Harmonic vibrational frequencies are computed by mass-weighting and diagonalizing the force constant matrix which is a matrix of second order derivatives of the electronic energy with respect to nuclear co-ordinates. Because the force constants are the underlying quantities, the firstly approach was to apply empirical scaling to force constants. This remains an effective approach. Another approach is uniform scaling of the harmonic vibrational frequencies. The resulting predictions are less accurate (more uncertain), but the latter approach has the advantage of simplicity [59].

The difficulties with the empirical force fields were overcome by the introduction of *ab-initio* quantum mechanical method of calculations. The wavenumbers calculated *ab-initio* by the Hartree-Fock (HF) method were, however consistently higher than the experimental wavenumbers of fundamentals by about 10% because of the neglect of electron- correlation and anharmonicity effects.

In order to solve these problems the scaled quantum mechanical (SQM) method was proposed by Pulay *et al*. [60, 61]. In this method the force constants of similar chemical fragments share the same scale factor. The values of scale factors are optimized by minimizing the weighted mean-square deviations of the calculated wavenumbers from the observed wave numbers [62].

The Density Functional Theory methods account for the correlational effects to a large extant; the calculated frequencies from DFT method are much closer to the experimental values. These can be scaled by Yoshida *et al*. [62, 63] who, based on a linear relationship between the scaling and vibrational wavenumbers, gave the expression:

$$\nu_{obs} = (1.0087-0.0000163\ \nu_{calc})\ \nu_{calc}. \qquad (56)$$

CONCLUSION

In this paper various approximations in solving the Schrödinger Equation have been discussed in details. Ab-inito, Density Functional Theory, Various Basis Sets and Scaling procedures have been discussed in detail which is very useful for theoretical study of vibrational spectroscopy of bio molecules. Computational methods can give useful information and help us to understand biochemical issues at molecular, atomic and even electronic level.

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