Chapter III

OVERVIEW OF COMPUTATIONAL TECHNIQUES AND NON-LINEAR OPTICAL CHARACTERIZATIONS

3.1 INTRODUCTION

Quantum chemical computational methods have become a promising tool for solving interesting chemical problems and reaction mechanism. It uses computers to generate information such as properties of molecules or simulated experimental results. It has become a useful way to investigate materials to make predictions before running the actual experiments that are too difficult or too expensive. Due to explosive developments in computer hardware and associated achievements, quantum mechanical methods can now be directly applied for various scientific applications. Computational quantum chemistry is primarily concerned with the numerical computation of molecular electronic structures by \textit{ab initio} and semi-empirical techniques. Computational methods, especially \textit{ab initio} have become a major tool in the study of molecular problems of structure, stability and reaction mechanism [215,216].

Some common computer software used for computational chemistry include:

- Gaussian'98
- GAMESS
- MOPAC etc.

Quantum chemical calculations provide useful data, which complements experimental data on the structures, properties and reactions of molecules. The calculations are based primarily on Schrödinger's equation and generate:
1. electronic and charge distributions
2. molecular geometry in ground and excited states
3. spectral wavenumbers (IR, Raman, NMR and UV/Vis spectra)
4. potential energy surfaces
5. thermodynamic calculations - heat of reactions, energy of activation and other observable properties (dipole moments, polarizability etc.)

These results are particularly useful for determination of properties that are experimentally inaccessible and interpretation of experimental data. In the present work Gaussian'98 package has been used for structural optimization and to find the related parameters for further understanding about the molecules considered. Hence, detailed information about the package and the experimental details are provided in this chapter.

3.2 METHODS IN COMPUTATIONS

For polyatomic molecules, the presence of several nuclei make quantum mechanical calculations more complex than for diatomic molecules. Moreover, the electronic wavefunction of a diatomic molecule is a function of the internuclear distance. In contrast, the electronic wavefunction of polyatomic molecules depends on several parameters, like bond distances, bond angles and dihedral angles of rotation about single bond [217]. A full theoretical treatment of a polyatomic molecule involves calculation of the electronic wavefunction for a range of each of these parameters.

There are two main approaches to calculate molecular structure and their reactivity. They are: (i) molecular mechanics and (ii) electronic structure theory [218].
3.2.1 Molecular Mechanics

In molecular mechanics simulations, laws of classical physics are used to predict the structures and properties of molecules. In this method, it does not explicitly treat the electrons in a molecular system. Instead, they perform computations based upon the interactions among the nuclei [219]. Electronic effects are implicitly included in force fields through parameterization. This method is a rather inexpensive computation and is used for very large systems containing many thousands of atoms. However, there are several limitations and the most important ones are,

i. Each force field achieves good results only for a limited class of molecules related to those for which it was parameterized. No force field can be generally used for all molecular systems of interest.

ii. Molecular properties which depend on suitable electronic details are not reproducible by molecular mechanics methods.

In this method the laws of quantum mechanics rather than classical physics are used as the basis for the computations [220].

3.2.2 Electronic Structure Methods

Electronic structure methods are based upon the fundamental laws of quantum mechanics, which states the energy, and other related properties of a molecule may be obtained by solving the Schrödinger equation.

\[
\left( -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \right) \psi (\rho_r, t) = \frac{i\hbar}{2\pi} \frac{\partial \psi(\rho_r, t)}{\partial t} \tag{3.1}
\]

where, ‘\(\psi\)’ is the wavefunction, ‘\(m\)’ is the mass of the particle, ‘\(\hbar\)’ is the Planck’s constant and ‘\(V\)’ is the potential field in which the particle is moving. For the
smallest systems, exact solutions to the Schrödinger equation are not computationally practical. Electronic structure methods are characterized by their various mathematical approximations to its solution. There are three major classes of electronic structure methods: viz. Semi-empirical methods, \textit{ab initio} methods and Density Functional methods [221].

i. Semi Empirical Method

Semi-empirical molecular quantum mechanical methods use a simpler Hamiltonian than the correct molecular Hamiltonian and use parameters whose values are adjusted to fit experimental data or the results of \textit{ab initio} calculations [222]. They solve an approximate form of the Schrödinger equation that depends on having appropriate parameters available for the type of chemical system under investigation. Semi-empirical methods may only be used for systems where parameters have been developed for all of their component atoms. They are relatively inexpensive and can be practically applied to very large molecules. Semi-empirical methods are appropriate for a variety of modeling tasks:

i. For very large systems, quantum mechanical methods are the only possible practical computations.

ii. For ground state molecular systems, the semi-empirical method can be well parameterized and well calibrated. In general, semi-empirical methods have been developed to focus on simple organic molecules.

iii. Qualitative information about a molecule such as molecular orbital, atomic charges or vibrational normal modes can be obtained. In some cases, semi-empirical methods may also be successfully used to predict energy trends arising from alternate conformations or substitute effects in a qualitative or semi-qualitative way.
In addition to this, semi-empirical models have a number of well-known limitations. They do not perform calculations about hydrogen bonding, transition structures, molecules containing atoms for which they are poorly parameterized, and so on [223]. One of the most commonly used semiempirical method is AM1, which is popular for modeling organic compounds. AM1 generally predicts the heats of formation more accurately. Depending on the nature of the system and information desired, AM1 will often give the more accurate results obtainable for organic molecules with semiempirical methods.

ii. *Ab Initio* Method

*Ab initio* calculations use the correct Hamiltonian and do not use experimental data other than the values of the fundamental physical constants [224]. A Hartree-Fock SCF calculation seeks the antisymmetrized products $\Phi$ of one-electron functions that minimizes $\int \Phi^* \hat{H} \Phi \, d\tau$, where ‘$H$’ is the true Hamiltonian and is thus an *ab initio* calculation indicates a calculation based on fundamental principles [225]. An *ab initio* molecular orbital calculation uses the approximation of taking $\psi$ as an antisymmetrized product of one-electron spin orbital and uses a finite (hence incomplete) basis set. Hartree-Fock theory is very useful for providing initial, first-level predictions for many systems. It is also reasonably good at computing the structures and vibrational frequencies of stable molecules and some transition states.

Semi-empirical methods are relatively inexpensive and provide reasonably qualitative descriptions of molecular systems and fairly accurate quantitative predictions of energies and structures for systems where good parameter sets exist. In contrast, *ab initio* computations provide high quality quantitative predictions for a broad range of system. They are not limited to any specific class
or size of a system [224]. It is a good base level theory, however neglect of electron correlation makes it unsuitable for some purposes.

iii. Density Functional Method

In 1964, Pierre Hobwenberg and Waltor Kohn [226] proved that the ground state molecular energy, wavefunction and all other molecular electronic properties of a molecules with a non-degenerate ground state can be uniquely determined by the ground state electron probability density $p_0(X, Y, Z)$, a function of only three variables. The ground state electronic energy ‘$E$’ is a function of ‘$p_0$’ ie, $E_0 = E_0[p_0]$ where the square brackets denote a functional relation. Density functional theory (DFT) attempts to calculate ‘$E_0$’ and other ground state molecular properties from the ground state electron density ‘$p_0$’ [227].

DFT analysis was originally formulated for a non-degenerate system in the ground state; there exists a one to one mapping between the external potentials and the electron densities. Once the electron density is known, the external potential and consequently the Hamiltonian, the wavefunction calculated may be used to determine the desired molecular properties. DFT calculations require about the same amount of computation resources as Hartee-Fock (HF) theory. DFT methods are attractive because they include in their model the effect of electron correlation and hence find ever-increasing popularity in the chemical community due to its capability to treat electron correlation with low computational cost as compared to correlated ab initio post-HF methods [228].

3.3 GAUSSIAN PROGRAM PACKAGE

Gaussian’98 is a connected system of programs for performing a variety of semi empirical and ab initio molecular calculations. Gaussian is capable of
predicting many properties of molecules and reactions including:

- Molecular energies and structures
- Energy and structure of transition states
- Vibrational frequencies
- IR and Raman spectra
- Thermochemical properties
- Bond and reaction energies
- Reaction pathways
- Molecular orbitals
- Atomic charges
- Multipole moments
- NMR shielding and magnetic susceptibilities
- Vibrational circular dichroism intensities

### 3.3.1 Basis Sets

A basis set is a mathematical description of the orbitals within a system used to perform theoretical calculations [229]. The basis set can be interpreted as restricting each electron to a particular region of space. Larger basis sets impose fewer constrains on electrons but require more computational resources. Standard basis sets for electronic structure calculations use linear combinations of basis functions (one-electron functions) to form the orbitals. An individual molecular orbital is defined as:

\[
\varphi_i = \sum_{\mu=1}^{n} C_{\mu i} \chi_{\mu}
\]  

(3.2)

where, \(\varphi_i\) is the \(i^{th}\) molecular orbital, \(C_{\mu i}\) are the coefficients of linear combination and \(\chi_{\mu}\) is the \(\mu^{th}\) atomic orbital and \(n\) is the number of atomic orbitals.

Gaussian and other *ab initio* electronic structure programs use basis
functions which are themselves composed of a linear combination of Gaussian functions; such basis functions are referred to as contracted functions and the component Gaussian functions are referred as primitives. A basis function consisting of a single Gaussian function is termed as uncontracted. The Gaussian program package [228] offers a wide range of predefined basis sets, which may be classified by the number and type of basis functions that they contain.

(i) Minimal basis sets contain the minimum number of basis functions needed for each atom. They use fixed-size atomic-type orbitals. The ST9-3G basis set is a minimal basis set.

(ii) Split valence basis sets, such as 3-21G and 6-31G have two (or more) sizes of basis function for each valence orbital and allow orbitals to change size, but not to change shape. Triple split valence basis sets like 6-311G, use three sizes of contracted functions for each orbital-type.

(iii) Polarized basis sets, by adding orbitals with angular momentum beyond what is required for the description of each atom in the ground state, allow orbitals to change the shape. The 6-31G(d) basis set also known as 6-31G* which contains d-functions added to the heavy atoms, is becoming very popular for calculations involving up to medium-sized systems.

(iv) Diffuse functions are large-size versions of s- and p-type functions (as opposed to the standard valence-size functions). They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions
are important for systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited states, systems with low ionization potentials, and so on. The 6-31+G(d) is the 6-31G(d) basis set with diffuse functions added to heavy atoms.

3.3.2 Geometry Optimization

Generally structural changes within the molecule produce differences in its energy and other properties. Its Potential Energy Surface (PES) specifies the way the energy of a molecular system varies with small changes in its structure. Potential energy surface (PES) is the mathematical relation linking molecular structure and energy. The minimum which corresponds to the lowest point in some limited region on the PES is the local minimum (Fig. 3.1). But global minimum is the lowest energy point anywhere on the PES. The point, which is

![Fig. 3.1 Potential energy surface diagram](image-url)
maximum in one direction and minimum in other direction is the saddle point. Saddle point corresponds to the transition structure between two equilibrium structures. The minimum specifies the equilibrium structure of the molecular system with different minima corresponding to different conformations. After finding the energy and gradient in some number of cycles, finally optimization gets completed when it has converged.

3.3.3 Frequency Calculations

IR and Raman Spectra

The first step in the vibrational spectral simulation is to form Hessian matrix ‘\( f_{\text{CART},ij} \)’ which holds the second partial derivatives of the potential ‘\( V \)’ with respect to displacement of the atoms in Cartesian coordinates (CART). The \( i,j^{th} \) element of the matrix is given by

\[
f_{\text{CART}}_{ij} = \left( \frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right)_0 \tag{3.3}
\]

This is a \( 3N \times 3N \) matrix (\( N \) is the number of atoms). Here \( \xi_1, \xi_2, \xi_3, \ldots, \xi_{3N} \) are used for the displacements in Cartesian coordinates \( \Delta x_1, \Delta y_1, \Delta z_1, \ldots, \Delta z_N \). The force constants are then converted in to mass weighted cartesian coordinates (MWC).

\[
f_{\text{MWC}}_{ij} = \frac{f_{\text{CART}}_{ij}}{\sqrt{m_im_j}} \left( \frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right)_0 \tag{3.4}
\]

Here, \( q_2 = \sqrt{m_1 \xi_2} = \sqrt{m_1 \Delta y_1} \) and so on, are the mass weighted Cartesian coordinates. A copy of \( f_{\text{MWC}} \) is diagonalised, yielding a set of \( 3N \) eigen vectors and \( 3N \) eigen values. The eigen vectors which are the normal modes are
discarded. The roots of the eigen values are the fundamental frequencies of the molecule.

**Scaling Procedures**

Hartree-Fock theory can predict IR and Raman frequencies with an overestimation of about 10-12% due to the neglect of electron correlation and anharmonicity. Thus, it is essential to scale the vibrational frequencies to produce good agreement with the experimental values. To find the optimum value of scaling factor, least square procedure is adopted [230].

Scaling factor can be determined by minimizing the residual $V = \sum_i^{all} (\nu_i^{\text{expt}} - \lambda \nu_i^{\text{theory}})$ resulting in:

$$\text{Scaling factor} = \lambda = \frac{\sum \nu_i^{\text{theory}} \nu_i^{\text{expt}}}{\sum (\nu_i^{\text{theory}})^2}$$

(3.5)

**Table 3.1 Scaling factors suitable for fundamental vibrations**

<table>
<thead>
<tr>
<th>Method</th>
<th>Scaling factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1</td>
<td>0.9532</td>
</tr>
<tr>
<td>HF/6-31G(d)</td>
<td>0.8953</td>
</tr>
<tr>
<td>HF/6-31G(d,p)</td>
<td>0.8992</td>
</tr>
<tr>
<td>HF/6-311G(d,p)</td>
<td>0.9051</td>
</tr>
<tr>
<td>MP2-fc/6-31G(d,p)</td>
<td>0.9370</td>
</tr>
<tr>
<td>B-LYP/6-311G(df,p)</td>
<td>0.9986</td>
</tr>
<tr>
<td>B-P86/6-31G(d)</td>
<td>0.9914</td>
</tr>
<tr>
<td>B3-LYP/6-31G(d)</td>
<td>0.9614</td>
</tr>
</tbody>
</table>

Applying the above set of procedure to a wide range of systems, the
scaling factors have been determined for different methods, some of which are tabulated in the above table (Table 3.1).

### 3.4 COMPUTATIONAL PROCEDURE

Quantum mechanical prediction of molecular properties has its wide use in chemical problems, owing to the development in computer hardware and efficient computational software. Numerous electronic structure programme packages are now available such as Gaussian, GAMES, Holdo and so on, among which the most commonly used software is Gaussian [228]. User-friendly graphics programs are now available using which we can visualize the output of the electronic structure calculations. Reliable assignments of vibrational spectra are possible by the visual inspection of vibrational modes, created by such programs. The commonly available visualization packages are MOLKEL, MOLDA, Gauss View, Chem Craft etc.

Gaussian is the most widely used program package for performing electronic structure calculations. Computations of optimized molecular geometry and vibrational spectra are normally carried out with input as the molecular structure provided in the Z- matrix format or in Cartesian co-ordinate form.

### 3.5 POPULATION ANALYSIS

Chemists are able to do research much more efficiently if they have a model for understanding chemistry. Population analysis is a mathematical way of partitioning a wavefunction or electron density into charges on the nuclei, bond orders, and other related information. These are probably the most widely used results that are not experimentally observable. Atomic charges cannot be
observed experimentally because they do not correspond to any unique physical property. In reality, atoms have a positive nucleus surrounded by negative electrons, not partial charges on each atom. However, condensing electron density and nucleus charges down to partial charges on the nucleus results in an understanding of the electron density distribution. Although this is an artificial assignment, it is very effective for predicting sites susceptible to nucleophilic or electrophilic attack and other aspects of molecular interaction. These partial charges correspond well to the chemist's view of ionic or covalent bonds, polarity, and so on [229,231].

3.5.1 Mulliken Population Analysis

One of the original and still most widely used population analysis schemes is the Mulliken population analysis [232-234]. The fundamental assumption used by the Mulliken scheme for partitioning the wavefunction is that the overlap between two orbitals is shared equally. This does not completely reflect the electro negativity of the individual elements. However, it does give one a means for partitioning a wavefunction and has been found to be very effective for small basis sets. For large basis sets, results can be very unreasonable. This is due to diffuse functions describing adjacent atoms more than they describe the atom on which they are centered. Mulliken analysis can assign an electron population to an orbital that is negative or more than two electrons. It also tends to underestimate the charge separation in ionic bonded systems.

In Mulliken analysis, the integrals from a given orbital are not added. Instead, the contribution of a basis function in all orbitals is summed to give the net population of that basis function. Likewise, the overlaps for a given pair of
basis functions are summed for all orbitals in order to determine the overlap population for that pair of basis functions. The overlap populations can be zero by symmetry or negative, indicating antibonding interactions. Large positive overlaps between basis functions on different atoms are one indication of a chemical bond.

Gross populations are determined by starting with the net populations for a basis function, then adding half of every overlap population to which that basis function contributes. The gross atomic population can be subtracted from the nuclear charge in order to obtain a net charge. Further analysis of overlap populations can yield bond orders.

### 3.6 NATURAL BOND ORBITAL (NBO) ANALYSIS

Natural bond orbital (NBO) analysis is an effective technique for studying hybridization and covalency effects in polyatomic wavefunctions, based on local block eigenvectors of the one-particle density matrix. NBOs are conceived as a "chemist's basis set" that corresponds closely to the picture of localized bonds and lone pairs as basic units of molecular structure. In the NBO analysis, the electronic wavefunction is interpreted as a set of occupied Lewis-type orbitals, paired with a set of formally unoccupied non-Lewis-type orbitals. The electronic interactions within these orbitals, the deviations from the Lewis electronic structure, and the delocalization effects can be interpreted as charge transfer between the filled Lewis orbitals (donors) and the theoretically empty non-Lewis orbitals (acceptors) [235]. The magnitude of these delocalization effects can be determined from an analysis of the off-diagonal elements in the Fock matrix in the
NBO basis by taking into account of all possible donor-acceptor interactions and then by calculating the strength of them by second-order perturbation theory.

The NBO for a localized ‘σ’ bond, ‘σ_{AB}’ between atoms A and B is formed from directed orthonormal hybrids h_A and h_B [natural hybrid orbitals (NHOs)].

\[ \sigma_{AB} = c_A h_A + c_B h_B \quad (3.6) \]

The natural hybrids in turn are composed of a set of effective valence-shell atomic orbitals [natural atomic orbitals (NAOs)], optimized for the chosen wavefunction. The important feature of the filled NBOs ‘σ_{AB}’ of the “natural Lewis structure” are both orthonormality and maximum occupancy, leading to describe the covalency effects in molecules. Similarly the NBOs ‘σ^{*}_{AB}’ that are unoccupied in the formal Lewis structure are used to describe the non-covalency effects.

\[ \sigma^{*}_{AB} = c_A h_A - c_B h_B \quad (3.7) \]

This antibonds ‘σ^{*}_{AB}’ arise from the same set of atomic valence-shell hybrids that make ‘σ_{AB}’ that represents the unused atomic valence space formally unsaturated by covalent bond formation. Small occupancies of these antibonds correspond to deviations from the idealized Lewis picture and thus to small non-covalent corrections to the picture of localized covalent bonds. The symbols ‘σ’ and ‘σ^{*}’ are formally used to refer to filled and unfilled orbitals of the formal Lewis structure, though the former may represent core orbitals (c), lone pairs (n), and ‘σ’ or ‘π’ bonds etc., and the latter may be ‘σ^{*}’ or ‘π^{*}‘ antibonds, extra-valence-shell Rydberg (r) orbitals, etc., according to the specific case. The interaction between filled orbitals of one subsystem and vacant orbitals of another subsystem can be used as a measure of the delocalization or hyperconjugation.
The hyperconjugative interaction energy can be deduced from the second order perturbation approach.

\[ E(2) = -n_\sigma \frac{\langle \sigma | F | \sigma \rangle^2}{\varepsilon_{\sigma^*} - \varepsilon_\sigma} = -n_\sigma \frac{F_{ij}^2}{\Delta E} \]  

(3.8)

where, \( \langle \sigma | F | \sigma \rangle^2 \) or \( F_{ij}^2 \) is the Fock matrix element between the i and j NBO orbitals and \( \varepsilon_\sigma, \varepsilon_{\sigma^*} \) are the energies of ‘\( \sigma \)’ and ‘\( \sigma^* \)’ NBOs and ‘\( n_\sigma \)’ is the population of the donor \( \sigma \)-orbital. The transfer of electron density between subsystems may be small but these values are chemically significant since 0.001 e of charge transfer is almost equivalent to 1 kcal mol\(^{-1}\) of the stabilization energy.

The NBO analysis involves a sequence of transformations from the input basis set to various localized basis sets [natural atomic orbitals (NAOs), hybrid orbitals (NHOs), bond orbitals (NBOs), and localized molecular orbitals (NLMOs)].

Input basis → NAOs → NHOs → NBOs → NLMOs

The localized basis sets may be subsequently transformed to delocalized natural orbitals (NOs) or canonical molecular orbitals (MOs). These steps are automatically performed by NBO computer program, which has been attached to a variety of \textit{ab initio} program packages such as GAUSSIAN, GAMESS, MOPAC, AMPAC, etc.

3.7 NON-LINEAR OPTICAL CHARACTERIZATIONS

Non-linear optics plays a major role in the technology of photonics to acquire, store, transmit and process informations. The ability to alter the
frequency of light to modulate the source of light and to alter the transmission characteristics through a medium are some of the nonlinear optical (NLO) phenomena observed in spectral investigations [28-33, 236]. Soon after the invention of the laser and the birth of the field nonlinear optics, second harmonic generation [237] and photon absorption were observed in a variety of organic molecules. Systematic studies of the relationship of molecular structure to molecular nonlinearities done during the 1970's brought out the importance of electron delocalization and charge transfer for high nonlinearity [238, 239].

Electro-optic, nonlinear optical and photorefractive materials are the active media which can be used in a variety of devices in which light waves have to be manipulated by electrical and optical fields [240-242]. Electro-optic materials which, in addition to the electric field induced changes of indices of refraction, also show photoconductivity and they have been shown to be efficient NLO materials. The optically released charge carriers from impurity ions can produce space-charge fields which lead to refractive index changes by the electro-optic effect [243, 244].

The electronic nonlinearities in organic materials are essentially based on molecular units containing highly delocalized π-electrons and additional electron donor and electron acceptor groups on opposite sides of the molecules. The NLO processes in π-electron organic and polymer systems have attracted considerable interest because, their understanding has led to new phenomena, new theoretical insights, new materials and devices. The π-electron excitations occurring on the individual molecular or polymer chain units are the basic origin of the observed non-resonant nonlinear optical phenomena. Higher level of understanding, in turn makes viable computer-aided molecular design of new
nonlinear optical chromophores. The development of photonics technology, however, relies largely on advances in fabricating new and better performing optical materials. Photonics is emerging as a multidisciplinary new frontier of science and technology that is capturing the imagination of scientists and engineers worldwide because of its potential applications to many areas of present and future information and image processing technologies [245-248].

3.7.1 Basic Aspects of Nonlinear Optical Phenomena

The interaction of light with a nonlinear optical material will cause the material characteristics to change and a variety of polarizations are induced depending on the frequency of radiation. When the frequencies are relatively low (radio wave and microwave) three contributions to the total polarization occurs; orientation polarization, vibrational polarization and electronic polarization. The first one involves reorientation of molecules in a field, whereas the second one is associated with the deformation of nuclear framework of the molecule by the applied field. When the radiation has wavelengths in the optical range, only electronic polarization occurs because of the higher frequencies involved.

The origin of nonlinear polarization is due to individual polarization which generates an internal electric field that modifies the applied electric field and the subsequent polarization and its inter-relationship. The first static hyperpolarizability ($\beta_0$) and its related properties ($\beta$, $\alpha_0$ and $\Delta\alpha$) have been calculated using the method HF/6-31G (d) based on finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field and the first hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be
reduced to 10 components because of the Kleinman symmetry [249]. The matrix can be given in the lower tetrahedral format. The components of ‘β’ are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, then

\[ E = E^0 - \mu_a F_a - 1/2 \alpha_{a\beta} F_a F_{\beta} - 1/6 \beta_{a\beta\gamma} F_a F_{\beta} F_{\gamma} + \ldots \ldots \] (3.9)

where, ‘E^0’ is the energy of the unperturbed molecules, ‘F_a’ is the field at the origin, ‘\( \mu_a \)’, ‘\( \alpha_{a\beta} \)’, ‘\( \beta_{a\beta\gamma} \)’ are the components of dipole moment, polarizability and the first hyperpolarizability respectively.

The total static dipole moment ‘\( \mu \)’, the mean polarizability ‘\( \alpha_0 \)’, the anisotropy of the polarizability ‘\( \Delta \alpha \)’ and the mean first hyperpolarizability ‘\( \beta_0 \)’, using the x-, y- and z- components are defined as:

\[ \mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \] (3.10)

\[ \alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \] (3.11)

\[ \Delta \alpha = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2} \] (3.12)

\[ \beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \] (3.13)

When the electric field associated with the electromagnetic radiation is small, as is usually the case with ordinary light, the polarization varies linearly with the electric field and the constant of proportionality is the familiar polarizability ‘\( \alpha \)’, in the case of molecules and the linear electric susceptibility ‘\( \chi^{(1)} \)’ in the case of bulk solids. However, when laser light is used, the associated electric fields are very large and the induced polarization is usually nonlinear (Fig. 3.2).
The total nonlinear polarization 'P' can be related to the permanent polarization 'P_0' and the applied electric field 'E' for the case of molecules and for bulk materials using the following equations, respectively.

\[ P_{\text{microscopic}} = P_0 + \alpha E + \beta E^2 + \gamma E^3 E + \ldots \]  

\[ P_{\text{macroscopic}} = P_0 + \chi^{(1)} E + \chi^{(2)} E^2 E + \chi^{(3)} E^3 E + \ldots \]  

\[ (3.14) \]  

\[ (3.15) \]

Fig. 3.2 Plot of induced polarization against applied field

where, 'α', 'β' and 'γ' are the molecular polarizability, first hyperpolarizability and second hyperpolarizability, respectively, and \( \chi^{(1)} \) is the susceptibility coefficient. The quadratic term gives rise to phenomena such as second harmonic generation and the linear electro-optic effect. The cubic term leads to effects such as third harmonic generation and the quadratic electro-optic effect.

Materials having a centre of inversion symmetry will have their induced polarization exactly reversed in direction when the electric field of the electromagnetic radiation is reversed i.e. \( P(-E) = -P(E) \). The quadratic and higher even order products of 'E', which contribute to the polarization are unchanged by
the change of direction of ‘E’, whereas the cubic and other odd order terms are reversed by the reversal of ‘E’. Hence, in centrosymmetric systems, the even order terms vanish completely and the nonlinear effects arise exclusively from cubic and higher order odd terms. On the other hand, in a non-centrosymmetric system there are no symmetry constraints which relate the polarizations in opposite directions and hence NLO effects of any order can be observed. It can be easily understood why the even order contributions to the nonlinearity disappear if centre of symmetry exists. For centrosymmetric molecules like benzene, the magnitude of induced dipole moments is independent of the direction (sign) of applied electric field.

\[ \mu_{\text{ind}} (+E) = - \mu_{\text{ind}} (-E) \]  
\[ \mu_{\text{ind}} (+E) = -\alpha E + \beta E.E + \gamma E.E.E. \]  
\[ \mu_{\text{ind}} (-E) = -\alpha E + \beta E.E - \gamma E.E.E. \]  

Owing to the fact that \( E.E \) is positive, irrespective of the sign of field \( E \), Equ. 3.18 can only be fulfilled for centrosymmetric molecules, if either \( \beta = 0 \) or if the field strength \( E = 0 \). This equation need not be satisfied by molecules possessing non-centrosymmetry.

### 3.7.2 Second Harmonic Generation

When a material is irradiated with a laser of frequency ‘\( \omega \)’, the response of the material can be expressed in the form of polarization equation. By substituting a field equation for \( E \), the nonlinear polarization ‘\( P \)’ can be modified as [250]:

\[ P = P_0 + \chi^1 E_0 \cos \omega t + \chi^2 E_0 E_0 \cos^2 \omega t \]
On simplification, the above equation transforms to:

$$P = P_0 + \frac{1}{2} \chi^2 E_0^2 + \chi^1 E_0 \cos \omega t + \frac{1}{2} \chi^2 \cos^2 \omega t$$  \hspace{1cm} (3.20)

The second order term gives a frequency independent contribution and other terms are frequency dependent. The former suggests that a DC polarization should appear in a second order NLO material when appropriately irradiated. This phenomenon is referred to as optical rectification. The latter term corresponds to the well-known effect in NLO, namely the frequency doubling or second harmonic generation (SHG), which is illustrated in Fig. 3.3.

![Fig. 3.3 Frequency doubling effect for optical communications](image)

### 3.7.3 Optimization of Second Order Polarizability ($\beta$)

In order to tailor optimal NLO materials, the origins of polarizability of a crystal must be understood which is generally composed of contributions from the lattice components (atoms, molecules) and the interaction between these components [251,252]. The optical nonlinearity of organic molecules can be increased by either adding conjugated bonds or by substituting donors and
acceptors. The large $\pi$-electron systems that can be easily moved upon application on electric fields and strong donor-acceptor substitutions are necessary for high optical molecular second-order nonlinearities. The important parameters influencing '\( \beta \)' are:

1. Donor-acceptor system
2. Nature of substituents
3. Conjugated $\pi$-systems
4. Influence of planarity

### 3.8 SECOND ORDER NONLINEAR OPTICAL EXPERIMENTS

The knowledge of the nonlinear optical second-order polarizabilities '\( \beta \)' provides insight into molecular structures and functional origins of second-order optical effects. It is important for the optimization of organic crystalline nonlinear optical properties. Comparison of molecular and crystalline second-order susceptibilities allows the determination of the influence of intermolecular interactions on the nonlinearity. Second-order nonlinear optical properties of organic materials are evaluated in terms of second-order nonlinear susceptibility $\chi^{(2)}$ and the first hyperpolarizability '\( \beta \)'. Second harmonic generation (SHG) efficiency either in terms of microscopic or macroscopic optical nonlinearity can be determined in solid using powders and thin films or in liquid form by dissolving dyes in an appropriate organic solvent.

#### 3.8.1 Kurtz - Perry Powder Method

Kurtz-Perry powder technique [253] can be used for screening materials to determine second-harmonic generation activity, which derives information
concerning angular averages of second-order nonlinear tensor components, coherence lengths and phase matching behavior. It is a screening technique to identify materials with non-centrosymmetric crystal structures and the capability for phase matching.

In this method, crystalline materials are reduced to powders and the particles are classified into particles sizes. The particles are packed into a thin cell of thickness 'l'. Addition of an index matching fluid can help reduce scattered light and put the experiment on a more quantitative footing. The sample cell is irradiated with a fundamental beam of diameter 'D' and the harmonic intensity in the forward direction is measured with a photomultiplier tube (Fig. 3.4). The results are compared with a signal from a urea reference standard. The cell and beam geometries are chosen so that a large number of particles relative to the average particle size 'r' are traversed by the beam. This implies that \( r = l = D \).

![Fig. 3.4 Kurtz-Perry arrangement to monitor the nonlinear optical phenomena](image)
In the case of very fine powders, where $\hat{r}$ is less than the average coherence length $\hat{l}_c$, the second-harmonic fields from the different particles are correlated with each other, provided that the particles are separated by a distance less than $\hat{l}_c$. The total intensity generated in the sample is given by,

$$I = \frac{\hat{r}}{\hat{l}_c^2} \left\langle (d^{2\omega})^2 \right\rangle \tag{3.21}$$

From this equation it is obvious that the harmonic intensity should increase as the particle size increases. For the phase-matched case, intensity should increase with increasing particle size. It is also clear that unless the particle size and coherence length are known, nothing can be concluded relative to the average nonlinear coefficient $d^{2\omega}$ of the material.

In the case where $\hat{r}$ is much greater than the coherence length $\hat{l}_c$, the situation becomes significantly different for the non-phase-matched and phase-matched cases. For the non-phase-matched case the total second-harmonic intensity is given by

$$I_{2\omega} \propto I_\omega \left( d_{pm}^{2\omega} \right)^2 l \tag{3.22}$$

Accordingly, the observed harmonic intensity is inversely dependent on particle size and goes to zero for very large particles.

If a material is phase matchable, the physical situation is quite different. The major fraction of the angular dependence is now associated with coherence length rather than the average nonlinear coefficient. The second-harmonic intensity is given by:
\[ I_{2\omega} \propto I_{(\omega)} \left( d_{pm}^{2\omega} \right)^2 l \]  

(3.23)

where, \((d_{pm}^{2\omega})^2\), is the value of the phase-matchable ‘d’ coefficient.

The powder technique enables to classify materials into three categories:

1. Materials in which the phase-matchable component is larger than the other component: noncentrosymmetric crystal structure.
2. Materials in which the non-phase-matchable component is larger than the other component: noncentrosymmetric crystal structure.
3. SHG inactive: centrosymmetric crystal structure.

It is easy to classify a material in class 3, since these materials do not exhibit any SHG in powder form. Furthermore, it is possible to determine whether material belongs to class 1 or class 2 by observing the powder SHG intensity as a function of particle size. The SHG intensity of a non-phase-matchable material is described by the following approximation:

\[
I_{(2\omega)} \propto d^2 l_c^2 I_{(\omega)} / 2\langle r \rangle, \quad (\langle r \rangle \gg l_c) 
\]  

(3.24)

\[
I_{(2\omega)} \propto d^2 l_{(\omega)}^2, \quad (\langle r \rangle \gg l_c) 
\]  

(3.25)

The SHG intensity of non-phase-matchable material decreases with the increase of averaging particle size \(\langle r \rangle\), when \(\langle r \rangle\) is larger than coherence length \(l_c\). In the case of phase-matchable, the SHG intensity does not decrease when \(\langle r \rangle\) is larger than \(l_c\).

3.9 CONCLUSION

Quantum chemical computations based on electronic structural methods viz. semi-empirical methods, \textit{ab initio} methods and density functional methods
have been discussed briefly. Moreover, molecular geometry, atomic charges and simulated vibrational spectra using Gaussian'98 software has been given for the detailed molecular structural and vibrational spectral analysis. Mullikens population analysis, natural bond analysis are discussed to explain the existence of strong intra- and inter-molecular hydrogen bonding. Kurtz-Perry technique used to determine the second harmonic generation in NLO active materials is also explained in detail.