Chapter – II

Procedure for Quantum Chemical Calculations
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ABSTRACT

The different stages involved in quantum chemical calculations are discussed. An overview of density functional theory and the different basis sets are outlined. Quantum mechanical procedure for the description of potential energy surface, single point energy calculations, normal co-ordinate analysis, TD/DFT for electronic spectra, hyperpolarisability calculations, natural bond orbital analysis (NBO), molecular electrostatic potential (MEP), NMR spectra and solvation models are discussed in detail.
CHAPTER-II

PROCEDURE FOR QUANTUM CHEMICAL CALCULATIONS

2.1. Introduction

Quantum mechanics is the basis for the most computational chemistry calculations. Computational chemistry involves the application of mathematical and the theoretical principles to the solution of chemical problems. Furthermore it is used as a tool by researchers to investigate molecular structure, properties, kinetics and reactivity. Computational techniques allow chemists to study chemical phenomena by simulation in silico using computers rather than complementary to examining compounds and reactions experimentally, calculations can be used both to predict the results of experiments and to assist in the interpretation of exciting results [1].

2.2. Computational chemistry

Computational chemistry simulates chemical structures and reactions numerically, based on the fundamental laws of physics. Nowadays advanced computer programs are used for performing quantum chemical calculations on a wide range of molecules. Quantum chemical calculations are an important complement for many experimental investigations in organic, inorganic, physical chemistry as well as atomic and molecular physics.

There are two broad areas within computational chemistry are molecular mechanics and electronic structure theory. They perform the following basic type of calculations:

A Computing the energy of a particular molecular structure (physical arrangement of atoms).
A Performing the geometry optimizations, which locate the lowest energy molecular structure in close proximity to the specified starting structure. Geometry optimizations depend primarily on the gradient of the energy and the first derivative of the energy with respect to atomic positions.

A Computing the vibrational frequencies of molecules resulting from interatomic motion with in the molecule. Frequencies depend on the second derivative of the energy with respect to atomic structure and frequency calculations may also predict other properties, which depend on second derivatives. Frequency calculations are not practically possible for all computational chemistry methods.

2.2.1. Molecular mechanics

Molecular mechanics simulations use laws of classical physics to predict the structures and properties of molecules. There are different molecular mechanics methods. Each one is characterized by its particular force field. These classical force fields are based on empirical results averaged over a large number of molecules. Because of this extensive averaging, the results can be good for standard systems; no force field can be generally used for all molecular systems of interest. Ignoring electrons in calculations, molecular mechanics methods cannot take care of chemical problems where electronic effects predominate.

2.2.2. Electronic structure methods

Electronic structure methods utilize the laws of quantum mechanics, which is the basis for computational calculations. Quantum mechanics states that the energy and other related properties of the molecule can be obtained by solving the Schrödinger equation,
However, exact solutions to the Schrödinger equation are not practical. Electronic structure methods are characterized by their various mathematical approximations and their solutions. There are two major classes of electronic structure methods. Semi-empirical methods employ simpler Hamiltonian by parameter values is adjusted to fit the experimental data. That means they solve an approximate parameters available for the type of chemical system of interest. There is no unique method for the choice of parameter. Ab initio force fields provide solutions to these problems.

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

2.2.3. Ab Initio methods

Ab initio orbital molecular methods are useful to predict harmonic force constants and frequencies of normal modes. Ab initio methods first optimize the molecular geometry and then evaluate the second derivative at the equilibrium positions usually using analytical derivatives. Such methods provide reliable values for harmonic vibrational frequencies for fairly large sized molecules. Additionally such calculations can be used to predict barriers to internal rotation as well as relative stabilities of different conformers. The information obtained from structural parameters, conformational stabilities, force constants, vibrational frequencies as well as infrared and Raman band intensities gives significant contributions to the field of vibrational spectroscopy.
Harmonic force constants in Cartesian coordinates can be directly derived from ab initio calculations. These force constants can be transformed to force constants in internal or symmetry coordinates. Ab initio calculations followed by normal coordinate analysis are very helpful in making reliable vibrational assignments. Band intensities from ab initio studies are another important output. Such band intensity data can also be very useful in making vibrational assignments. Two principally different quantum mechanical methods addressing the vibrational problems are namely Hartree-Fock method and Density functional theory (DFT). Density functional theory calculation has emerged in the past few years as successful alternative to traditional Hartree-Fock method. The DFT methods, particularly hybrid functional methods have evolved as a powerful quantum chemical tool for the determination of the electronic structure of molecules [2-5]. In the framework of DFT approach, different exchange and correlation functional are routinely used. Among these, the Becke-3-Lee-Yang-Parr (B3LYP) combination is the most used since it proved its ability in reproducing various molecular properties, including vibrational spectra, electronic transitions, nonlinear optical activity (NLO), NMR chemical shifts, molecular electrostatic potential [6-7]. The combined use of B3LYP functional and various standard basis sets, provide an excellent compromise between accuracy and computational efficiency of molecular properties, vibrational spectra, electronic transitions, NMR chemical shifts, NLO properties and natural bond orbital analysis (NBO) for large and medium size molecules. The vibrational frequencies calculated by applying DFT methods are normally overestimated than experimental values by 2-5% on an average. This
overestimation is due to the neglect of electron correlation, anharmonicities and incomplete basis sets.

This overestimation can be narrowed down by applying empirical corrections called scaling, where the empirical scaling factors are ranging from 0.8 to 1.0. The scaling factors depend on both method and basis sets and they partially compensate for the systematic errors in the calculation of frequencies. Global scaling or uniform scaling, multiple or selective scaling are some scaling methods advocated to minimize the overestimation of the frequency differences. Ab initio calculation could be performed using Guassian 03 software package [8].

If the quantum-mechanical force field is not corrected, especially in the case of large deviations from the experimental results, this omission can complicate the theoretical analysis of the vibrational spectrum of the molecule and lead to the errors in the assignment of the experimental frequencies. Therefore, determining empirical corrections to quantum mechanical force fields is important. It is shown that among all the methods for empirically correcting quantum-mechanical force fields, the one with the best physical basis is the modern version of the Pulay method [9-11].

2.2.4. Density functional theory

Density functional theory is a quantum mechanical method used to investigate the electronic structure of many body systems in particular, molecules and the condensed phases. Density functional theory is the most popular and versatile methods available in condensed matter physics and computational chemistry. Traditional methods in electronic structure theory particularly Hartree-Fock theory is based on the many electron wave function. The main objective of
density functional theory is to replace the many body electronic wave functions, which is the function of electron density.

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

Fig.2.1. Flow diagram of program used in the quantum chemical calculations

Whereas the many body wave functions is dependent on 3N variables, three spatial variables for each of the N electrons, the density is only a function of three variables and is a simpler quantity to deal with both conceptually and practically.

Although density functional theory has its conceptual roots in the Thomas Fermi model, density functional theory was put on a firm theoretical footing by Hohenberg kohn theorems. The first theorem demonstrates the existence of a one to one mapping between the ground state electric density and the ground state wave
function of a many particle system. The second theorem proves that the ground state
density minimizes the total electronic energy of the system. The most common
implementation of density functional theory is through the Kohn-Sham method.
Within the frame work of Kohn-Sham DFT, the intractable many body problems of
interacting electron in a static external potential is reduced to a tractable problem of
non interacting electrons moving in an effective potential. The effective potential
includes the external potential and the effects of the coulomb interactions between
the electrons, such as the exchange and correlation interactions.

Despite recent improvements, there are still difficulties in using density
functional theory to suitably describe intermolecular interactions, especially Van der
Waals forces (dispersion), charge transfer excitations, transition states, global
potential energy surfaces and some other strongly correlated systems; and in
calculations of the band gap in semiconductors. Its incomplete treatment of
dispersion can adversely affect the accuracy of DFT (at least when used alone and
uncorrected) in the treatment of systems which are dominated by dispersion (e.g.
interacting noble gas atoms) or where dispersion competes significantly with other
effects (e.g. in biomolecules) [12-13]. The development of new DFT methods
designed to overcome this problem, by alterations to the functional or by the
inclusion of additive terms is a current research topic [14-17].

2.2.5. Derivation and formalism of DFT

Normally in many-body electronic structure calculations, the nuclei of the
treated molecules or clusters are seen as fixed (the Born-Oppenheimer
approximation), generating a static external potential V in which the electrons are
moving. A stationary-electronic state is then described by wave functions $\psi(r_1, \ldots, r_N)$ fulfilling the many electrons Schrödinger equation,

$$
\psi = [T + V + U] = \left[ \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^N V(r_i) - \sum_{i<j}^N U(r_i, r_j) \right] \psi = E \psi
$$

(2.2)

Where $H$ is the electronic molecular Hamiltonian, $N$ is the number of electrons and $U$ is the electron – electron interaction. The operators $T$ and $U$ are so-called universal operators because they are the same for any system, while $V$ is system dependent or non-universal. As one can see, the actual difference between a single particle problem and the much more complicated many-particle problem arises from the interaction term $U$. There are many sophisticated methods for solving many-body Schrödinger equation based on the expansion of the wave function in Slater determinants. While the simplest one is the Hartree-Fock method, more sophisticated approaches are usually categorized as post-Hartree-Fock methods. However, the problem with these methods is the huge computational effort, which makes it virtually impossible to apply them efficiently to larger, more complex systems.

Here DFT provides an appealing alternative, and versatile as it provides a way to systematically map the many-body problem with $U$, onto a single-body problem without $U$. In DFT the key variable is the particle density $n(r)$ which is given by,

$$
n(r) = N \int d^3 r_2 \int d^3 r_3 \ldots \int d^3 r_N \psi^*(r_1, r_2, \ldots, r_N) \psi(r_1, r_2, \ldots, r_N)
$$

(2.3)

Hohenberg and Kohn proved in 1964 [18] that the relation expressed above can be reversed, i.e. to give ground state density $n_0(r)$ it is in principle to calculate the corresponding ground state wavefunction $\psi_0(r_1, \ldots, r_N)$. 

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In other words $\psi_c$ is a unique functional of $n_0$, i.e.

$$\psi_0 = \psi_c[n_0]$$  \hspace{1cm} (2.4)

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

$$\langle O[n_0] = \langle \psi_0[n_c]|O|\psi_c[n_0] \rangle$$  \hspace{1cm} (2.5)

in addition, the ground state energy is a functional of $n_0$, it can be revealed from the following equation

$$E_0 = E[n_0] = \langle \psi_0[n_0]|T + V + U|\psi_0[n_c] \rangle$$  \hspace{1cm} (2.6)

where, the contribution of the external potential $\langle \psi_0[n_0]|V|\psi_c[n_0] \rangle$ can be written explicitly in terms of the density,

$$V[n] = \int V(\vec{r})n(\vec{r})d^3r$$  \hspace{1cm} (2.7)

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

$$E[n] = T[n] + U[n] + \int V(\vec{r})n(\vec{r})d^3r$$  \hspace{1cm} (2.8)

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

The variational problem of minimizing the energy functional $E[n]$ can be solved by applying the Lagrangian method of undetermined multipliers, which was done by Kohn and Sham in 1965 [19]. The functional in the equation (2.8) can be written as a fictitious density functional of a non-interacting system.

$$E_0[n] = \langle \psi_0[n]|T_0 + V_0|\psi_0[n] \rangle$$  \hspace{1cm} (2.9)
Where \( T_s \) denotes the non-interacting kinetic energy and \( V_s \) is an external effective potential in which the particles are moving. Obviously, \( n_s(\vec{r}) = n(\vec{r}) \) if \( V_s \) chosen to be

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

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

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \tag{2.10}
\]

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

\[
n(\vec{r}) \mathbb{W}_s(\vec{r}) = \sum_i^{N} |\phi_i(\vec{r})|^2
\]

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

\[
V_s = V + \frac{\int \frac{e^2 n_e(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 \vec{r}'}{\int n_e(\vec{r})} + V_{xc}[n_e(\vec{r})] \tag{2.11}
\]

where the second term of equations (2.11) denotes, Hartree term describing the electron Coulomb repulsion, while the last term \( V_{xc} \) is called exchange correlation potential. Here, \( V_{xc} \) includes all the many-particle interactions. Since the Hartree term and \( V_{xc} \) depend on \( n(\vec{r}) \), which depends on the \( \phi_i \). From these values a new density can be calculated and the whole process is started again. The procedure is then repeated until convergence is reached.

2.2.6. Applications of DFT

Kohn-Sham theory can be applied in several distinct ways depending on the parameters being investigated. In molecular calculations, a huge variety of exchange-correlation functionals have been developed for chemical applications. A popular functional widely used is B3LYP which is a hybrid method in which the
DFT exchange functional, is combined with the exchange functional from Hartree-Fock theory [6,7,20]. These hybrids functional carry adjustable parameters, which are generally fitted to a training set of molecules.

2.3. Basis set

The basis set is the mathematical description of the orbital within a system used to perform the theoretical calculation. Larger basis sets more accurately approximate the orbital by imposing fewer restrictions on the locations of the electrons in space. When molecular calculations are performed, it is common to use basis composed finite number of atomic orbitals, centred at each atomic nucleus within the molecule. Most molecular quantum mechanical methods initiate the calculation with the choice of a set of basis functions. The use of an adequate basis set is an essential requirement for success of the calculation.

Standard basis sets for electronic structure calculations use linear combinations of Gaussian functions to form the orbital. To accurately represent an AO, we must use a linear combination of several Gaussians. Gaussian offers a wide range of pre-defined basis sets, which may be classified by the number and types of basis functions that they contain.

2.3.1. Minimal basis sets

The most common minimal basis set is STO-XG, where X is an integer. This X value represents the number of Gaussian primitive functions comprising a single basis function. In these basis sets, the same numbers of Gaussian primitives comprise core and valence orbital. Minimal basis sets typically give rough results that are insufficient for research quality publication, but are much cheaper than their larger counterparts. Commonly used minimal basis sets of this type are:
2.3.2. Split valence basis sets

In most of the molecular bonds, the valence electrons are mainly taking part in the bonding. In recognition of this fact, it is common to represent valence orbital by more than one basis function (each of which can in turn be composed of a fixed linear combination of primitive Gaussian functions). Since the different orbital of the split have different spatial extents, the combination allows the electron density to adjust its spatial extent appropriate to the particular molecular environment. Minimum basis sets are fixed and are unable to adjust to different molecular environments. The notation for these split-valence basis sets is typically X-YZG. In this case, the presence of two numbers after the hyphens implies that this basis set is a split-valance double-zeta basis set. The commonly used split-valence basis sets are:

- 3-21G
- 3-21G*-polarised
- 6-31G
- 6-31+G*
- 6-311+G*
- 6-311++G*
2.3.3. Correlation-consistent basis sets

Some of the most widely used basis sets are developed by Dunning and coworkers, since they are designed to converge systematically to the complete-basis-set (CBS) using extrapolation techniques. For first- and second-row atoms, the basis sets are cc-pVNZ where N=D, T, Q, 5, 6,.. (D=double, T=triples, etc.) and 'cc-p', stands for ‘correlation-consistent polarized’, ‘V’ indicates they are valence-only basis sets. They include successively larger shells of polarization (or correlating) functions (d, f, g, etc.). More recently these 'correlation-consistent polarized' basis sets have widely used for Hatree Fock methods. Examples of these basis sets are

- cc-pVDZ - Double-zeta
- cc-pVTZ - Triple-zeta
- cc-pVQZ - Quadruple-zeta
- cc-pV5Z - Quintuple-zeta, etc.
- aug-cc-pVDZ, etc. - Augmented versions of the preceding basis sets with added diffuse functions

These basis sets can be augmented with core functions for geometric and nuclear property calculations and with diffuse functions for electronic excited-state calculations, electric field calculations and long-range interactions such as Van der Waals forces. The steps for constructing additional augmented functions exist in the literature; as many five augmented functions have been used in second hyperpolarizability calculations. Because of the precise construction of these basis sets, extrapolation can be done for several molecular properties.
2.4. Gaussian

GAUSSIAN-03 is a computational chemistry software program used for performing the quantum chemical calculations. It is well-known, the Gaussian program is widely-used electronic structure programs for advanced quantum chemistry research and other fields.

2.5. Gauss view

Gauss view is an affordable full featured graphical user interface for Gaussian-03. With the help of gauss view, one can submit the inputs to Gaussian and to examine the output graphically which are generated by Gaussian-03 software. Gauss view incorporates an excellent molecule builder. One can use it to rapidly sketch the molecules and possibly view three dimensional molecular pictures. It is used to build an atom, ring group, amino acids and nucleic acids. Gauss view can graphically display a variety of Gaussian results such as animation of the normal modes, molecular orbital, atomic charges, electrostatic potential, NMR shielding density and potential energy surface scans.

2.6. Geometry optimization

Optimization of molecular geometry is a first step in quantum chemical calculation. This is mostly done on an isolated molecule in the gas phase. Geometry optimization is performed to locate the lowest energy molecular energy structure in close proximity to the specified starting structure.

A geometry optimization will adjust the atomic arrangements in a molecule until an energy minimum is reached. This is the lowest position on the potential energy surface. Optimized geometry is generally used to compare with experimental data. In the absence of experimental data construction of models is based on
intuitively reasonable values for bond distances, inter-bond angles and dihedral angles. Fig. 2.2 shows a typical flow chart explaining the geometry optimization process.

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Method of calculation, basis set, molecular geometry

- Initial guess, charge, spin multiplicity

- Trial wave functions estimated from semi-empirical calculations

- SCF calculation of energy and improved wave function

- Has energy converged?

- Is the geometry optimized, i.e., are the forces within the molecules sufficiently close to zero?

- Determine a better guess of Molecular geometry

- Output

  Vibrational spectra, Electronic transitions, NLO property, MEP, NBO and NMR spectra

- Calculate molecular properties

- Optimized geometry

Fig. 2.2. Flowchart illustrating the steps involved in quantum chemical calculations of molecular structures and properties

2.7. Potential Energy Surface (PES)

The Potential energy surface (PES) is a hypersurface defined by the potential energy of a collection of atoms over all possible atomic arrangements. In actual practice, PES is a mathematical relationship linking molecular structure and the resultant potential energy. For a diatomic molecule, it is a 2D plot with the inter-nuclear separation on the X axis (the only way that the structure of such a molecule can vary), and the energy at that bond distance on the Y axis, producing a curve. For
larger systems the surface has many dimensions, as molecules have different degrees of freedom.

2.8. Frequency calculations

Vibrational spectra of molecules in their ground and excited states can be computed by employing the Gaussian program. Frequency calculation are valid only at stationary points on the potential energy surface, for this reason it is necessary to run a geometry optimization prior to doing a frequency calculation. In addition to predicting the frequencies and intensities of spectra, the program can also describes the displacements of the molecule as it undergoes normal modes of vibrations. Molecular frequencies depend on the second derivative of energy with respect to the position of nuclei. Analytic second derivative are provided by the Hartree-Fock, density functional theory (B3LYP), Moller Plesset (MP2) and CASSCF theoretical procedures. An optimized energy is used as input for the frequency calculation. The frequency calculations should be performed using the same theoretical model and the basis set as the one that was used to obtain the optimized geometry of the molecule [21-25]. Harmonic force fields derived from quantum mechanics are widely used at present for the calculation of frequencies and the modes of normal vibrations [26,27]. This opened the way to calculate the frequencies and intensities of spectral bands with a minimum degree of arbitrariness and finding the rational explanations for a number of chemical and physical properties of substances.

However, in numerous current quantum-mechanical calculations of vibrational spectra performed at different levels of approximation, calculated frequencies are higher than their experimental counterparts. This outcome is due to the more or less systematic overestimation of the force constants as in the Hartree-
Fock method [28]. This overestimation of the force constants depends on the basis set employed [28] and to the discrepancies in applications of the Moller-Plesset theory [29]. These calculations required empirical corrections. To improve agreement with experiment, quantum-mechanical force fields are corrected in one way or another, e.g. using empirical corrections called scale factors which are estimated from the experimental vibrational spectra of small molecules with reliable frequency assignments.

2.8.1. Normal coordinate analysis

Detailed description of vibrational modes can be studied by means of normal coordinate analysis. Normal coordinate analysis is a procedure for calculating the vibrational frequencies which relates the observed frequencies of preferably the harmonic infrared and Raman frequencies to the force constants, equilibrium geometry and the atomic masses of the oscillating system. A normal coordinate analysis has proven useful in assigning vibrational spectra but its predictive ability depends on reliable intramolecular force constants.

2.8.2. Classification of normal modes

By applying Group theory, the point group symmetry of the molecule and normal modes of vibrations are classified according to the irreducible representations. Further these vibrations are distributed to various symmetry species to which they belong. Applying IR and Raman selection rules, the number of genuine vibrations under each species is determined.

2.9. Single point energy calculations

Single point energy gives a prediction of the energy of a molecule with specific geometry. This is usually followed by a Mulliken population analysis which
is used to estimate the charge distribution. Electrostatic moments are also calculated, which then allow to calculate the dipole moments. Single point energy calculations can be performed at any level of theory, with small or large basis sets.

2.10. Electronic Spectra and TD/DFT

Electronic spectra are the basis for many chemical –physical molecular features [30]. Computations can easily analyze the different chemical-physical effects by modulating the spectral properties of the molecule. Many interesting chemical problems involve in both the ground and excited states of molecules. Density functional theory (DFT) has provided a successful description, only for ground state properties of atoms, molecules and solids. Therefore DFT formalism has to be extended to excited states in order to describe photochemical and photophysical processes. Time-dependent DFT (TDDFT) has become an effective tool for excited state calculations [30]. TDDFT provides first principles method for the calculation of excitation energies and many related response properties within a density functional framework.

For a molecule, there is typically one or more low energy excited states that can be described as valence-MO-valence-MO single electronic excitations, and reproduced in the spectra. The calculation of multiplet energies requires the energies of excited determinants, such as occupied spin-orbital number i to the empty spin-orbital number j, to be computed. Thus certain states are referred to as $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions. Finding wave functions for these states is sometimes facilitated by their relatively simplicity of the character. The time-dependent generalization of the DFT formalism offers a rigorous route to the calculation of the dynamic response of charge density. This allows the determination of the electronic excitation spectrum
in the usual dipole approximation, since the poles of the dynamic polarizability determine the excitation energies [31]. The strengths of the poles are given by the oscillator strengths $f_i$, or equivalently, by the transition dipole moment $\mu_i$, i.e the intensity of the optical transitions.

2.11. Hyperpolarizability calculations

Molecules with large nonlinear optical responses, for instance the first hyperpolarizability are preferred in order to improve the efficiency of manipulating photonic signals, such as changing the photon frequencies. The external electric field is incorporated in the Hamiltonian equations they are frequently referred as Finite-Field approach. In these formulations, the molecular Hamiltonian explicitly included a field term (-$r$.F), which describes the interaction between the external static field and the electronic structure. At any given field strength, the molecular wave function is found, from which the appropriated expectation values of the field dependent molecular energy ($E(F)$) and the field-dependent dipole moment ($\mu(F)$) can be evaluated by following equations

$$E(F) = \langle \psi(F) | H(F) | \psi(F) \rangle$$

$$\mu(F) = \langle \psi(F) | \sum a_i(F) r_i(F) | \psi(F) \rangle$$

The relationship between the $\mu$ of a molecule interacting with an external field and the NLO response can be given as

$$\mu_i(F) = \mu_i \sum a_{ij} F_j + \sum \beta_{ijk} F_j F_k + \sum \gamma_{ijkl} F_j F_k F_l + \ldots$$

where $\mu_i$ is the dipole moment in the absence of the field, the hyperpolarizability of increased order is obtained by differentiating $\mu(F)$ with respect to the field.
The partial derivative of the polarization ($P_i$) with respect to the field can give the polarizability, while the second partial derivative of the polarization gives $\beta$ and third partial derivative gives $\gamma$ evaluated at zero field [32].

$$\alpha_{ij} = (\partial \mu_i / \partial F_j)_{F=0}$$  \hspace{1cm} (2.15)

$$\beta_{ijk} = (\partial^2 \mu_i / \partial F_j \partial F_k)_{F=0}$$  \hspace{1cm} (2.16)

$$\gamma_{ijkl} = (\partial^3 \mu_i / \partial F_j \partial F_k \partial F_l)_{F=0}$$  \hspace{1cm} (2.17)

Similarly the $\alpha$, $\beta$, $\gamma$ coefficients can be obtained from the molecular energy expansion [32] as follows. The molecular dipole moment is the negative field derivative of the energy. Thus

$$\mu_i = -(\partial E / \partial F_i)$$  \hspace{1cm} (2.18)

$$\alpha_{ij} = -(\partial^2 E / \partial F_i \partial F_j)_{F=0}$$  \hspace{1cm} (2.19)

$$\beta_{ijk} = -(\partial^3 E / \partial F_i \partial F_j \partial F_k)_{F=0}$$  \hspace{1cm} (2.20)

$$\gamma_{ijkl} = -(\partial^4 E / \partial F_i \partial F_j \partial F_k \partial F_l)_{F=0}$$  \hspace{1cm} (2.21)

The relationships given for $\alpha$, $\beta$ and $\gamma$ are valid for the static field limit. Thus, the majority of derivative based NLO response computations have been reported at zero frequency. Numerical differentiation strategies [33] are used to compute the above derivatives. Pulay and others [34-36] have developed analytic gradient techniques to compute the above derivatives. Generally in finite field method analytical gradients techniques are used to compute NLO and other properties.

2.12. Natural bond orbital analysis (NBO)

NBO localization is a multistep process the details of which are sufficiently complicated, but a general overview of the procedure can be described here. In an initial step, orbitals that are associated almost entirely with a single atom, e.g., core orbitals and lone pairs, are localized as so-called natural atomic orbitals (NAOS).
Next, orbitals involving bonding (or antibonding) between pairs of atoms are localized by using only the basis set AOs of those atoms. Finally, the remaining Rydberg-like orbitals are identified, and all orbitals are made orthogonal to one another. The result is that, except for very small contributions from other AOs to ensure orthogonality, all NAOs and Rydberg orbitals are described through the basis-set AOs of two atoms. Thus, NBO analysis provides an orbital picture that is as close as possible to a classical Lewis structure for a molecule.

This localization scheme permits the assignment of hybridization both to the atomic lone pairs and bond orbitals. Hybridization is a widely employed and generally useful chemical concept even though it has no formal basis in the absence of high-symmetry constraints. With NBO analysis, the percent s and p character (d, f etc.) is obvious from the coefficients of the AO basis functions, from which the NAO or NBO is formed. In addition, population analysis can be performed using the NBOs to derive partial atomic charges.

Another useful chemical concept is hyperconjugation, which rationalizes certain chemical phenomena in terms of filled-orbital-empty-orbital interactions. NBOs analysis can be used to quantify this phenomenon. Since the NBOs do not diagonalize the Fock operator, when the Fock matrix is formed in the NBO basis, off-diagonal elements will be non-zero. Second-order perturbation theory gives the off-diagonal elements between filled and empty NBOs, and can be recognized with the stabilization energies obtained from hyperconjugation [37].

2.13. Molecular electrostatic potential (MEP)

The molecular electrostatic potential surface (MEP) is a plot of electrostatic potential mapped on the iso-electron density surface, simultaneously displays
molecular shape, size and electrostatic potential values for the molecules. The electrostatic potential has been used primarily for predicting sites and relative reactivities towards electrophilic attack, and in studies of biological recognition and hydrogen bonding interactions [38, 39]. A multipole expansion is a computationally suitable single-center formalism, which allows one to quantitatively compute the degree to which a positive or negative test charge is attracted to or repelled by the molecule that is being represented by the multipole expansion. This quantity, the molecular electrostatic potential (MEP), can be computed exactly for any position \( r \) as

\[
V_{\text{MEP}}(r) = \sum_{k}^{\text{nuclei}} \frac{Z_k}{|r-r_k|} - \sum_{r,s} \int \frac{1}{|r-r'|} \varphi_s(r') \psi(r') \, dr
\]  

(2.22)

Note that this assumes no polarization of the molecule in response to the test charge. The MEP is an observable, although in practice it is rather difficult to design appropriate experiments to measure it. Computationally, it is usually evaluated within the formalism of either HF or DFT theories, in which case one may write

\[
V_{\text{MEP}}(r) = \sum_{k}^{\text{nuclei}} \frac{Z_k}{|r-r_k|} - \sum_{r,s} P_{rs} \int \frac{1}{|r-r'|} \varphi_s(r') \varphi_r(r') \, dr
\]  

(2.23)

where \( r \) and \( s \) run over the indices of the AO basis set, \( P \) is the one-electron density matrix its appropriate analog for UHF and DFT, and the orbitals \( \varphi \) are those comprising the basis set.

The MEP is particularly useful when visualized on surfaces or in regions of space, since it provides information about local polarity. Typically, after having chosen some sort of region to be visualized, a color-coding convention is chosen to depict the MEP. For example, the most negative potential is assigned to be red, the most positive potential is assigned to be blue, and the color spectrum is mapped to
all other values by linear interpolation. If this is done on the molecular van der waals surface, one can immediately distinguish regions of local negative and positive potential, which may be informative for purposes of predicting chemical reactivity.

Mapping of the electrostatic potential to grid points in three dimensions has also proven useful for comparative molecular field analysis. This procedure is used to identify common features in the electrostatic potentials of several molecules when the goal is to correlate such commonality with another chemical property, e.g. pharmaceutical activity. In the latter instance, a group of molecules having high activity are oriented about a common origin and the electrostatic potential of each is evaluated at each grid point. A subsequent averaging of the values at every point may identify key regions of positive or negative potential associated with activity and that information may be used for the design of future drug candidates.

For very large molecules the ESP can be very useful for analyzing function, but direct calculation from quantum mechanics is restricted to fairly low levels of theory. An alternative method that shows promise is to assemble the full molecular density from high-level calculations on small constituent fragments.

2.14. NMR spectral properties

NMR measurements calculate the energy difference between a system in the presence and absence of an external magnetic field. For a chemical shift measurement on a given molecule there are two magnetic fields of interest, the external field of the instrument and internal field of the nucleus. The chemical shifts are proportional to the second derivative of the energy with respect to these two fields, and by using second derivative of the energy the chemical shifts can be computed. However, the integrals in the equation are more complex because, unlike
the electric field, which perturbs the potential energy term of the Hamiltonian, the
magnetic field perturbs the kinetic energy term. The nature of the perturbed kinetic
energy operator is such that an origin must be specified defining a coordinate system
for the calculation. This origin is called the ‘gauge origin’. The magnetic field is
independent of the choice of the gauge origin. Thus may perhaps compute magnetic
properties if the wave function used is exact. For HF wave functions, one can also
achieve independence of the gauge by using an infinite basis set, however that is
hardly a realistic option.

To reduce artifacts associated with the gauge origin, two different
approaches have seen extensive use in the literature. The older method employs
gauge-including atomic orbitals (GIAOs) as a basis set [40]. By a clever
incorporation of the gauge origin into the basis function themselves, all matrix
elements involving the basis functions can be arranged to be independent of it. An
alternative is the ‘individual gauge for localized orbitals’ (IGLO) method, where
different gauge origins are used for each localized MO in order to minimize
error [41]. Of the two methods, modern implementation of GIAO is probably
somewhat more robust, but it is possible to obtain good results from both the
methods. A different problem associated with NMR chemical shifts for heavy atoms
is the influence of relativistic effects.

2.15. Solvation models

One can carry out accurate gas-phase calculations and then make broad
generalization about how the surrounding condensed phase may influence the
results. The condensed-phase effects are small for the particular properties being
studied, but it is useful in a qualitative sense. To determine nature of the medium
one must consider solvation process. Different physical effects contribute to the overall solvation process the most important components of solvation process are electrostatic interactions, cavitation, change in dispersion and changes in bulk solvent structure. Several solvation models are available in quantum mechanical procedures each have definite merits. The integral equation formalism (IEF) solvation method involves solutes in a liquid phase, using the permittivity \( \varepsilon \) for characterization of the solvent. IEF solvation model is a member of the PCM group implemented in Gaussian version 03, it has become the default PCM formulation [42]. In IEF, the potentials are redefined in terms of the proper Greens functions \( G(x,y) \) is the potential produced in \( x \) by a unit point charge located in \( y \). However, in several cases the Green function can be effectively built numerically, and thus the IEF approach can be generalized to many other environments as, for example, a diffuse interface with an electric permittivity depending on the position. Various spectroscopic techniques were employed for the present work, the instrumentation of FT-IR, FT-Raman, UV and FT-NMR are discussed in the next chapter.
References


