Chapter 2

Methodology: Experimental Techniques and Computational Simulation
2.1 Introduction:

This study covers an extended range of experimental and computational spectroscopic techniques. For the understanding of the upcoming chapters, it is very crucial to have idea about some fundamental methodological tools. In this chapter, necessary information about used techniques are furnished. The first section, we introduce sample preparation and basics of experimental techniques. The second section deals with the theoretical background of computational electronic structure calculations.

2.2 Experimental techniques:

This section contains the sample preparation methods and instrumental details. The study has been performed using various type of samples, including liquid and thin film samples.

2.2.1 Sample preparation:

Since the fluorescence is a highly sensitive method, extreme precautions have to be taken into account, while preparation and handling of the samples. Even the fingerprints in the cuvette can cause anomaly in the measurement of fluorescence parameters by the instruments. All the molecules of interest and solvents used in this study were of spectroscopic grade quality and purchased from Sigma Aldrich USA. The details regarding purification, polymer films preparation, nanoparticles coating and solution phase sample preparation is provided in the respective chapters. Quantitative measurements of the samples were done by electrical micro-balance Danwer Scales (India) Pvt. Ltd. having least count 1000 μgm.

The spectroscopic measurements are widely performed in two fundamental modes namely steady state measurements and time domain measurements.

2.2.2 Steady state measurements:

The steady state measurements are ascribed to the wavelength dependent measurement of radiation. The radiation absorbed and emitted by the molecules, studied by absorption spectrum, excitation spectrum and emission spectrum are put under the steady state measurements.

2.2.2 (a) Steady state Absorption measurements:

The absorption spectra of the compounds of interests were recorded at room temperature with the help of JSACO V-670 double beam spectrophotometer (JASCO instruction manual; 2010). The photographs of this spectrophotometer are shown in figure 2.1.
This spectrophotometer uses a single monochromator design and is capable of measuring the wavelength range from 190 nm to 2500 nm. The monochromator features automatically exchangeable dual gratings system. The grating contains 1200 grooves/mm for the UV/VIS region and 300 grooves/mm for the NIR region. For the measurement in UV/VIS region, this spectrophotometer uses a PMT detector and a Peltiercooled PbS detector is provided for the NIR region. The spectrophotometer includes a deuterium discharge lamp for UV region measurements and tungsten lamp for use in the visible and IR region. The grating monochromator, mounted on a Czerny–Turner mount, disperses the light to produce monochromated beam. This monochromated light is set to fall on a sector mirror, which splits the light into two paths, one of these passes through the sample and the other passes through the reference sample cell. The cuvette cells are usually made of quartz, glass or plastic. The light, after absorption process is detected using PMT and PbS detectors (as wavelength of interest) and the output of detector is fed to the computer. The obtained graphs can be analyzed by Spectra Manager™ II software. The block diagrams of the optical and electrical configuration of the system are given in figure 2.2.
Figure 2.2 Simplified schematic diagram of a typical UV/Vis spectrophotometer.

The errors like detector response, light fluctuation in source, change in the amplifier gain and other anomalies are corrected through the ratio recording method. The absorption spectrum is produce according to the famous Bear-Lambert Law. The various photo-physical parameters viz. oscillator strength \( f \), molar extinction coefficient \( \varepsilon \) and natural radiative lifetime \( \tau_0 \) etc. of different electronic states, can be estimated with the help of following relations through absorption spectrum.

\[
f = 4.33 \times 10^{-9} \int \varepsilon \bar{\nu} \tag{2.1}
\]

\[
\varepsilon_\lambda = \frac{\text{Optical density}}{\text{Concentration} \times \text{path length}} = \frac{\log I / I_0}{C \times L} \tag{2.2}
\]

\[
\tau_0 = \frac{3.47 \times 10^8 g_m}{n^2 \bar{\nu}^2_{\text{max}}} \frac{1}{g_n} \int \varepsilon \bar{\nu} = \frac{1.5}{\bar{\nu}^2_{\text{max}} \times f} \tag{2.3}
\]

Where \( \int \varepsilon \bar{\nu} \) is the integrated area under the absorption band, \( n \) is reflective index of the medium, \( \bar{\nu} \) is the wave number of absorption maximum, \( g_m \) and \( g_n \) are the multiplicity of the states.

2.2.2 (b) Steady State Fluorescence and Excitation Measurements:

The emission and excitation spectra measurement of the compounds were performed with Edinburgh’s spectrofluorometer FLS-900 (Instruction Manual of FLS900, 2011), at room temperature. The photograph of this instrument is given in table 2.3.
Emission spectrum is a plot of total number of quanta emitted with respect to different wavelength (or wavenumber/frequency) by exciting the fluorophore at a fixed desired wavelength obtained from absorption spectrum. The quantum yield “\( \phi \)” (number of quanta emitted / number of quanta absorbed) of the fluorophore is calculated by ratio recording method\(^1\), using Quinine sulphate dication in water as a standard (\( \phi = 0.55 \)) given as:

\[
\frac{F_1}{F_2} = \frac{I_0 \, c_2 \, I_2 \, \phi_2}{I_1 \, c_1 \, I_1 \, \phi_1} = \frac{\text{Area 2}}{\text{Area 1}} = \frac{\phi_2 \, \text{Optical Density 2}}{\phi_1 \, \text{Optical Density 1}} \quad (2.4)
\]

Thus the relative quantum yield of the fluorophore was calculated by relation:

\[
\phi_2 = \phi_1 A_1 F_2 n_2^2 / A_2 F_1 n^2. \quad (2.5)
\]

Where ‘1’ corresponds to standard for reference and ‘2’ implies for sample. ‘A’ is the absorbance and ‘F’ is the integrated fluorescence intensities of the sample and reference. Correction of refractive index ‘n’ of the sample solution is also taken into account.

The excitation spectrum is a plot of intensity variation of fluorescence emission against the different wavelength or wave number of the exciting light. It depends on \( \varepsilon \) and \( \phi \) of the fluorophore as\(^1\)–\(^6\):

\[
F = \phi I_a = \phi I_0 [1 - e^{-2.3 \varepsilon c l}] \quad (2.6)
\]

Where \( c \) is concentration, ‘\( l \)’ is path length of the sample and \( \varepsilon \) is the molar absorption coefficient.

The radiative lifetime or radiative rate through fluorescence steady state measurements, can be calculated as
\[
\frac{1}{\tau_F} = K_F = 2.88 \times 10^{-9} n^2 \frac{\int F(\bar{\nu})d\bar{\nu}}{\int \bar{\nu}^{-1} F(\bar{\nu})d\bar{\nu}} \frac{\int \epsilon d\bar{\nu}}{\bar{\nu}}
\]  

(2.7)

Where \( n \) is the average refractive index, \( \int F(\bar{\nu})d\bar{\nu} \) is the integrated area of the total fluorescence band, \( \bar{\nu} \) is wave number (cm\(^{-1}\)) of maximum intensity and \( \int \epsilon d\bar{\nu} \) is the integrated area of the first absorption band. The expression assumes that there is no configuration change takes place on excitation or the absorption and fluorescence are mirror symmetry corresponds to each other.

The block diagram of a typical spectrofluorometer is shown in figure 2.4 and detail of these components are given below following four components

**Figure 2.4 Block diagram of a typical spectrofluorometer.**

(i) **Continuous Light Source (Xenon Lamp)**

For the steady state fluorescence measurements, normally light source used is 450W xenon arc lamp. This lamp produces radiation of continuous wavelengths. The white light thus produced has an optimal spectral range from less than 250 to more than 1000 nm. For excitation at a particular wavelength monochromators are used.
(ii) **Monochromator:**

A monochromator is an arrangement to select a narrow band of wavelengths out of a wider range of wavelengths. Spectrofluorometer consists of two monochromators viz. excitation monochromator and emission monochromator. The grating of monochromator determines the spectral coverage and resolution, optical throughput efficiency (grating optimization wavelength/blaze) and polarization effects. For single grating excitation and emission monochromator, the groove density is typically 1800 groove/mm, wavelength coverage and dispersion are 200-900nm and 1.8nm/mm respectively. These the entrance and exit slits of the monochromaters are computer controlled. Schematic diagram of the monochromators used in FLS900 shown in Figure 2.5.

![Figure 2.5 Schematic diagram of single-grating monochromator.](image)

(iii) **Sample Chamber**

In the sample chamber, two access ports are provided for routine access to the sample or any component inside the compartment. A circular lid is provided on the top of the chamber. To protect the detector against ambient light, both the access ports are interlocked. If any of the two lids is opened, the shutter in the emission monochromator will automatically close the detector. An additional slot on the top of the sample chamber accepts a filter holder for the excitation beam. This does not need to be interlocked as the aperture is small, which allows a minimal amount of the ambient light into the sample compartment. The whole of interior of the sample chamber is
covered with a highly absorbing, suitable optical grade black paint. Different sample holder for liquid, solid and polymer films were used for experiment of interest. The sample compartment used in FLS900 are shown in figure 2.6.

![Figure 2.6 Sample compartment of FLS900.](image)

A horizontal slit of variable width is used to attenuate the amount of light reaching at the sample. This is called attenuator. An attenuator reference detector provided behind the attenuator. The light through the reference detector helps to correct the excitation spectra.

(iv) **Detector**

High-gain photomultiplier (PMT) R 928 detectors are used in spectrofluorometer FLS-900, which are suitable for measurements in both the steady state and time-resolved applications. PMTs, operating in photon-counting mode offer the highest sensitivity in the spectral range from 200 nm to 1700 nm. Analogue detectors are used for measurements above around 1700 nm.

**2.2.2 (c) Time Resolved Measurements:**

Since, steady state measurements provide the averaged data of emission process in wavelength or energy scale, many information are lost because of averaging. The time resolved measurements offer much greater approach to extract information about kinetics of inter and intra molecular processes\(^\text{16}\) in the excited state. The fluorescence lifetime/decay time \((\tau)\) of a molecule can be defined as the depopulation rate of excited states. The time required for the fluorescence
intensity to be decreased up to 1/e\textsuperscript{th} of its initial value is called \textit{fluorescence lifetime} as shown below Scheme I

**Scheme I**

The de-excitation process for an electronically excited molecule (M\textsuperscript{*}) typically happens via radiative and non-radiative events with rate constant $K_r$ and $K_{nr}$ respectively. The rate of de-excitation in terms of rate constants can be given as following equation:

$$\frac{d[M^*]}{dt} = -(K_r + K_{nr})[M^*] = -K_f[M^*] \quad (2.8)$$

Taking the Dirac delta excitation pulse, the concentration of excited molecules $|M^*|_t$, at any instant $t$, can be articulated from equation (2.8) as:

$$|M^*|_t = |M^*|_0 e^{-K_f t} \quad (2.9)$$

where $|M^*|_0$ is the initial concentration per unit volume of the excited molecules. Similarly, the emission intensity at time $t$ is expressed as

$$I_t = I_0 e^{-K_f t} \quad (2.10)$$

In contemporary methods, two kinds of techniques are widely used for fluorescence lifetime measurement. These are known as pulse fluorometry (in time domain) and phase modulation (in frequency domain). In present study, the time domain measurements were also carried out with Edinburgh instruments FLS900 system having time correlated single photon counting (TCSPC) card and a pulsed light source. For lifetime measurements, usually the sample is excited with a pulse of light of fixed wavelength and the fluorescence signal originated from the
sample pass through the emission monochromator at a fixed wavelength and collected by single photon counting PMT, which converted this fluorescence signal to electrical signal and reached as stop signal in Time to amplitude converter (TAC) of TCSPC card. A direct signal from the pulsed light source start the TAC, which generate a voltage that increases linearly with time. While the fluorescence signal due to a single detected photon stop the TAC, in the TCSPC card as shown in figure 2.7.

![Block diagram for TCSPC technique and TCSPC card](image)

**Figure 2.7** Representation of (a) Block diagram for TCSPC technique and (b) TCSPC card.

Proper attenuation is used in order to restrict the stop pulse rate to ~1% of the start (to make the event single photon counting). The time difference between start and stop pulses are measured with a time-to-amplitude converter (TAC) device, which is considered as the heart of the single photon counting (SPC) instruments. Higher stop rate may lead to pulse pile up and hence error is produced in decay (O’Connor D.V. et al., 1984). The output of this device generates a voltage, which is proportional to the time between these two events. If no photon is detected during the TAC range (which is adjusted) the devices resets to zero. The output from the TAC is then fed to analog to digital converter and finally to a multi-channel pulse height analyzer (MCPHA). The procedure is repeated until a large number of photons have been detected typically 10^5 or more. The number of times each voltage was generated by the TAC is represented in histograms from by MCPHA as shown in figure 2.7. A time evolution of fluorescence intensity is observed as shown in scheme I and this becomes the experimentally measured decay curve. However, the above decay is distorted by lamp pulse, optical and detecting devices. In order to extract the true decay function of the sample it is required that the exciting pulse must be a δ-pulse and the detected
electronics must be very fast. However, since the instrumental response using PMT RS900 is typically 500 Pico-second using pico-second laser, it is required that, in order to extract true sample decay the deconvolution of the measured decay with the instrumental decay profile is necessary. The instrumental decay is measured separately by tuning both monochromators to the same wavelength and replacing the sample with a scatterer (milk powder in water). The least square re-convolution method with nonlinear $\chi^2$ minimization technique (Imhof R.E. et al., 1982) were used to analyze the decay data. The procedure for the data analysis is given below.

(i) **Data Analysis:**

The time resolved measurement is all about determining the impulse response function $F(t)$, which is a pulse of width much shorter than decay time of the sample but usually, the widths of pulses are comparable to the sample decay time. This situation makes it hard to define the zero time point and hence the $1/e$ from zero time point. Moreover, for the many of the cases, decay profile is not a single exponential decay. Thus, it again makes the meaning of the $1/e$ point absurd. For the correction of pulse width, the instrumental pulse $L(t)$ is measured. This measurement is done just after or before fluorescence decay measurement since the excitation profiles may vary with time or environmental conditions. $L(t)$ measurement is performed using a solution which scatters light e.g. magnesium oxide ($\text{Mg}_2\text{O}$). The convolution of instrumental pulse with the sample impulse response (Joshi G.C. et al., 1986; Birch D.J.S. et al., 1985). $D(t)$, provides decay of fluorescence.

Thus, if the decay component $D(t)$ is shorter or comparable to the instrumental response, Thus when the decay component $D(t)$, is comparable or shorter than the $L(t)$. The obtained decay fit $F(t)$, will not be the true decay profile of the sample. The true decay function is obtained by convolution and compare method using following equation (Lakowicz J. R., 1991):

$$F(t) = \int_0^t D(t')L(t - t')dt'$$  \hspace{1cm} (2.11)

Where $F(t)$ is the measured fluorescence decay after convolution, $D(t)$ represents true fluorescence profile, $L(t-t')$ is the lamp profile distorted by the instrumental detection. $t'$ is variable time delay (channel number) of extremely small width $dt'$ known as ‘channel width’. The reconvolution technique for the single exponential decay is shown in following scheme II:
So simple exponential decay can be written as

\[ F(i) = L(i) \otimes \frac{1}{\tau} \exp\left(-\frac{1}{\tau}\right) \]  

(2.12)

Where \( \otimes \) is the convolution symbol. On comparing it with equation:

\[ F(i) = A + B.F(i + \Delta) \]  

(2.13)

Where \( i \) is the number of data channels, \( A \) is noise background, \( B \) is scaling factor, \( \Delta \) is shift parameter and \( \tau \) is decay time. Taking the impulse response as a sum of exponentials

\[ F(t) = \sum_{i} \alpha_i e^{-\frac{t}{\tau_i}} \]  

(2.14)
The values of $\alpha_i$ and $\tau_i$ are varied until the best fit is obtained. The ‘goodness of fit’ is judged by $\chi^2$-test, which is calculated as:

$$\chi^2 = \sum \omega_i [R(t) - R_C(t)]$$

(2.15)

Where $R_C(t)$ is the calculated value and is used to compare with the observed values $R(t)$, $\omega_i = 1/R(t)$ is a statistical weighting factor to handle the expected error in $R(t)$ values (Torre S., 1983).

In this thesis, the whole of the time domain measurements were performed by high frequency nano second pulsed laser or LED of desired wavelengths.

(ii) **Precautions and Sources of Error in TCSPC:**

TCSPC is a very promising technique with wide dynamic range and it can be used to study even low quantum yield samples. However, it needs several aspects to keep in mind while performing an experiment:

- **Pulse pile-up:** To keep the concept of SPCT valid, the count rate must not be too high (<2%) so that not more than one STOP photon occurs during the seep of TAC.

- **PMT color effects:** The time shifts due to the difference in detection and excitation wavelengths must be eliminated by trial and error time-shifting method.

- **Sample geometry:** There is a great chance of error in reconvolution if geometry of the scatterer is not as that of the sample. It needs very careful effort while recording the lamp profile. A 1 cm of distance can cause time difference of nearly 30 ps.

2.2.2 (d) **Vacuum coating unit:**

The Hind Hivac™ vacuum coating unit model No. 12A4D was used to deposit thin film of silver nano particles on the quinine sulphate doped polyvinyl alcohol film, to understand the plasmonic effect of silver nano particles on the photophysics of quinine sulphate and its protonated species as discussed in chapter 5. This coating unit consists of 0.4 m diffusion pump supported by oil sealed rotary pump. Within a 0.3 m diameter steel bell jar, the ultimate pressure can be obtained of the order of $8\times10^{-6}$ mbar in this unit. It has electron beam and flash evaporation setups. In general, the evaporation is made at a pressure of $(1-2) \times 10^{-5}$ Torr. The Pirani gauge (in the range $0.5\times10^{-3}$ Torr) and Penning Gauge (in the range $10^{-2}$ to $10^{-6}$ Torr) are employed to measure the pressure in the system. The schematic diagram of the coating system is shown in the figure 2.8.
Figure 2.8 Representation of (a) typical vacuum coating unit; (i) Schematic coating arrangement (ii) Representation of coating process and (iii) Schematic diagram of entire coating unit. (b) Photograph of Hind Hivac” vacuum coating unit model No. 12A4D.

A digital thickness monitor (model number DTM-101) having a temperature controller cum monitor is provided to show the interior temperature (30°C) during the coating and a display setting, to show the coating rate. The whole coating unit is put in a vacuum vessel where coating material is kept on furnace and a substrate containing circular disc (rotating holder) of metal is mounted just above the furnace. A high voltage supply enables furnace to evaporate the coating material and thus substrate attached to rotating holder gets coated.

2.2.2 (e) **X-ray photoelectron spectroscopy (XPS) Measurements:**

X-ray photoelectron spectroscopy (XPS) was used for the study of the effect of charge transport from the quinine sulphate and its dication doped PVA film to Ag nano-particles by a change in binding energy through the model Kratos Analytical, SHIMADZU group company AMICUS XPS UK. If a material is irradiated by monochromatic x-rays, photoelectrons are emitted from the surface of material. The characteristic of the element of the irradiated sample can be obtained from the kinetic energy of these emitted electrons. The chemical state of an atom causes changes the binding energy (BE) of a photoelectron which in turns changes kinetic energy (KE) of
photoelectrons. The relation between BE and the KE of photoelectron can be given by the simple equation; \( \text{BE} = h\nu - \text{KE} \) where \( h\nu \) is the photon (x-ray) energy. XPS measurements provide elemental and chemical state information virtually of all types of material. The schematic diagram of XPS setup used in the study of BE of Ag nano-particles is shown in figure 2.9.

![Figure 2.9](image1.png)  
**Figure 2.9** The schematic diagram of XPS measurement.

The AMICUS is recognized as a versatile x-ray photo-electron spectrometer. Its compact design enables it to be used for a wide range of applications. The incorporation of the "Dupont" type analyzer along with optimized digital electronics makes the AMICUS an instrument of high performance. It is fully software controlled setup with 10 sample carousel and the sample of the dimension \( \leq 10\text{mm diameter} \leq 5\text{mm thick} \) can be used. AMICUS uses Mg/Al anodes/conical formed magnesium target as x-ray source of 300W max power at 12kV and 25mA. For the detection of photoelectrons the single channel electron detector is used. XPS measurements of Ag transition in with and without silver nano island coated films are described in chapter 5 to understand the effect of surface plasmon of Ag metal nano particles on the photophysics of quinoline and its protonated species.

![Figure 2.10](image2.png)  
**Figure 2.10:** The AMICUS.
2.3 **Computational spectroscopy and Electronic Structure Calculations:**

In this section, techniques of quantum chemical simulations, used to obtain all the ground and excited state information, including geometry optimizations, and state specific calculations to generate electronic/ vibronic absorption and emission spectra have been discussed. The results obtained from these calculations are important to understand the finer detail of the molecule in ground and excited state and nature of the different properties of the molecules, which are difficult to study experimentally.

The quantum chemical methods developed to study the properties of molecules can be broadly classified into three categories: (I) Valence bond (VB) theory, (II) Molecular orbital (MO) theory and (III) Density functional theory (DFT). VB theory uses the chemical concepts of bond formation, provides it a quantum mechanical description and explains bonding of small molecules nicely. However, it overestimates electron correlation and its application to large systems is not quite convenient due to which it is not popular for practical applications. MO theory uses linear combinations of atomic orbitals (LCAO) to represent molecular orbitals. Electrons are assigned to molecular orbitals according to the Pauli Exclusion Principle and total wave functions are expressed by determinants. Its application is straightforward due to which, it is dominantly used to study different types of problems. However, as such, MO theory underestimates electron correlation but provisions exist to correct for the same. The MO theory can further be classified into two sub-categories: (i) Semi-empirical MO methods, where an approximate Hamiltonian is used and many integrals are neglected while other integrals are evaluated in terms of parameters the values of which are adjusted to fit experimental data. These methods are computationally economical, can be employed to study large systems but usually the results obtained are approximate. (ii) Ab-initio MO methods, where all the integrals are calculated and usually, if due care is taken, the results obtained are quite reliable. (iii) DFT is based on electron density, includes electron correlation to a good extent, is computationally economical and different molecular properties can be obtained fairly reliably using it (Hohenberg, P., 1964; Kohn, W., 1965; Parr, R. G., 1989; Koch, W., 2001). It is the most popular method for practical applications at present.

Nowadays, there is a variety of quantum chemical software available to carry out the computational work. We have used *Gaussian 09* suite of programming package to estimate the molecular, structure and spectroscopic properties. This software package offers a number of approaches like semi-empirical, Hartree-Fock (HF), Møller–Plesset perturbation theory, DFT etc
to deal with the molecular system. This software package helps us to find the energies, molecular parameters, molecular structures and vibrational frequencies of molecular systems along with the various aspects of spectroscopic properties. Apart from this, electronic structures of molecule in gas or liquid phase, reaction sites in molecular system, stable geometries, reaction pathways and thermo-chemical parameters can also be obtained by Gaussian 09. Gauss view 05 has been used to visualize the computed results. DFT and time dependent (TD)-DFT methods have been used to explain the absorption and emission experimental results.

2.3.1 Density Functional Theory

Since, Hartree-Fock theory deals with many electron wave function, the correlation energy term was ignored because of computational expenses. Density functional theory (DFT) offers an efficient solution to this problem. It is an electronic structure theory which deals with the ground electron density distribution \( \rho(r) \) instead of many electron wave function. Now the required coordinates for system having N electrons was reduced from 3N to just 3. This modification brought much convenience in computing the electronic structure properties.

In DFT formalism, we take the electronic energy \( E_{el} \) as a functional of the total electron density \( \rho(r) \)

\[
E_{el} = E_{el}[\rho(r)]
\]  
(2.16)

The idea of introducing the energy of a system as a function of total electron density was proposed by Thomas (Thomas, L. H., 1927) and Fermi (Fermi, E., 1927). According to Thomas and Fermi model, the kinetic energy expression, based on the uniform electron gas treatment, can be expressed as a function of \( \rho(r) \) as follows:

\[
T_{TF}[\rho(r)] = \frac{3}{10} (3\pi^2)^{2/3} \int [\rho(r)]^{5/3} dr
\]  
(2.17)

Combining it with the classical expression for the (Electron-electron) repulsive potential, and the (nuclear-electron) attractive potential, it can be written as:

\[
T_{TF}[\rho(r)] = \frac{3}{10} (3\pi^2)^{2/3} \int [\rho(r)]^{5/3} dr - Z \int \frac{\rho(r)}{r} dr + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr dr'
\]  
(2.18)

The last two terms in the above equation are correspond to the potential energy parts arising due to nuclear-electron and electron-electron interactions respectively. What is called DFT process nowadays, is nothing but same idea applied by Slater (Slater, J. C., 1951) in 1951, in order to
develop the Hartree-Fock-Slater method. P. Hohenberg and W. Kohn (Hohenberg, P., Kohn, W., 1964) proposed two theorems in 1964 that are the mainstay of the modern DFT.

The calculation of effective atomic charges is significant whenever quantum-chemical calculations are applied to molecular systems, because they affect dipole moment, molecular polarizability and electronic structure. In such systems, the atomic charges are attributed through population analysis. In order to study electrostatic arguments that would explain the probable structure and reactivity of the molecule of interest. An electron density distribution analysis has been performed on the basis of atomic charges determined by Mulliken Population Analysis (MPA), Hirshfeld Population Analysis (HPA) and Natural Population Analysis (NPA) charge schemes in the gas or liquid phase, at B3LYP/6-31G(d,p) level of theory.

2.3.2 Time-Dependent Density Functional Theory (TD-DFT)

TDDFT is a very promising method to treat time-dependent many-electron quantum mechanics. This has been a popular method because of its practical balance between computational accuracy and computational cost (Runge E., E. K. U. Gross., 1984; Rappoport D. et al., 2005; Burke K. et al., 2005). Practically, TDDFT utilizes a non-interacting reference system of electrons, termed as “Kohn-Sham” system (W. Kohn and L. J. Sham1965). The Runge-Gross and van Leeuwen theorems are the backbone of TDDFT. We start with a time dependent Hamiltonian of system of N electrons within Born-Oppenheimer (Born, M. and Oppenheimer, R., 1927) approximation described as:

$$\hat{H}(t) = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^2 + \sum_{i<j}^{N} \frac{1}{|r_{i} - r_{j}|} + \sum_{i} v_{ext}(r_{i}, t)$$

(2.19)

In practice the exact solution to the equation (2.20) is not available because of its complexity. TD-DFT offers time dependent density as a reduced variable:

$$i \frac{\partial}{\partial t} \Psi(r_{1}, r_{2}, r_{3}, \ldots r_{N}, t) = \hat{H}(t)\Psi(r_{1}, r_{2}, r_{3}, \ldots r_{N}, t)$$

(2.20)
\[ \rho(r, t) = N \int d^3 r_2 \ldots d^3 r_N |\Psi(r_1, r_2, r_3 \ldots r_N, t)|^2 \]  

(2.21)

The density is quite convenient to use instead of wave function because it provides the normalization probability of an electron at any instance \( t \) and position \( r \) in wave function based evaluations, the conditional probability is obtained for \( N \) electron simultaneously at position \( r_1, r_2, r_3 \ldots r_N \) at time \( t \).

It appears that many information might have been lost because of replacement of wave function by density but the Runge-Gross theorem establishes the fact that the density essentially contains the same information as the many body wave function does.

2.3.3 (a) **Basis Sets and Basis Functions**

In quantum chemistry, the molecular systems are represented as the linear combination of atomic orbitals and the basis sets are the mathematical representation of these orbitals (Levine, I. N., 1994; Koch W., 2001). For the computational process it is necessary to select the appropriate basis set.

The different types of basis sets are discussed below

2.3.3 (b) **Minimal basis set**

These kind of basis sets are represented as STO-\( n \)G (\( n=2, 3\ldots 6 \)). In such basis sets a single function is used for one STO. Here, only one Slater type orbital is used to define an atomic orbital (single zeta). If one takes \( n<3 \), the results obtained are poor and thus STO-3G is called minimal basis set. The minimal basis sets are used either for qualitative result or for giant molecular system.

2.3.3 (c) **Split valence basis set**

The split valence basis sets are usually employed to study the organic molecules, these are also known as Pople basis set. In these basis sets, valence shell are taken to be split in more than one STOs and number of GTOs are adjustable for the core electrons and valence electron separately. Notation for such basis sets are given as [(core)-(Inner valence shell)(outer valence shell)]G. For example: 3-21G consists 3 GTOs for core electrons, 2 GTOs for inner valence shell and1 GTO for outer valence shell. Similarly, 6-31G, 6-311G are double zeta and tripal zeta split valence basis sets, respectively.
2.3.3 (d) Polarization and diffusion functions:
Split valence basis sets usually do not consider the variation of orbital shape. The inclusion of polarization function enables the basis sets to consider the change in orbital shape by taking angular momentum into account. For this, \( d \) (or simply \( * \)) can be added for heavy atoms and to take polarization into account for Hydrogen atoms \( p \) (or \( ** \)) can be added to the Pople basis sets, e.g. 6-31G(d) or 6-31G*, 6-31G(d,p) or 6-31G**. Practically, the orbital exponents do not fall abruptly, therefore the Gaussian functions with small exponents (0.01 to 0.1) are used. These are specified by ‘+’ sign, e.g. 6-31+G*, 6-31++G*. Single ‘+’ implies that diffusion effect is added on other than hydrogen atoms while ‘++’ adds diffusion effect to the hydrogen atoms as well.

2.3.4 Molecular Properties
As it is mentioned in the beginning of this section that Gussian 09 is capable of calculating a number of molecular properties, such as optimized geometries, vibrational frequencies, conformational search, different charge distributions, dipole moments, molecular electrostatic potentials (MEP), electronic absorption and emission spectra with vibronic details, IR and Raman spectra, NMR spectra and many more (Neese F., 2009) Few out of these properties are discussed below, which are used in the present work in the forthcoming chapters.

(a) Molecular Geometry
The optimization of the molecular geometry is to find the structure corresponding to global minimum in potential surface. It is accomplished by a systematic minimization of the total energy with respect to the internal coordinates (viz. bond lengths, bond angles and dihedral angles). True minimum is confirmed by the absence of imaginary frequency. Optimized geometry provides true bond length, bond angle and other parameters.

(b) Dipole Moment
The dipole moment is a measure of the asymmetry of charge distribution in the molecular system, and is written as a vector in three components x, y and z. Dipole moment in Gaussian is given in units of Debye. It can be calculated directly from the nuclear coordinates and the electronic wavefunction.

(c) Molecular electrostatic potential surfaces
One of the most important information obtained from quantum calculation is Molecular Electrostatic Potential (MEP). The MEP is created in the space around a molecule by its nuclei
and electrons, and it is basically mapping of electronic density and determines the sites for electrophilic, nucleophilic reaction and hydrogen-bonding interactions. The red region represents the negative potential for a proton (attractive region) and blue region shows positive potential region for the proton. A typical example is shown in following figure.

![Image](image.png)

**Figure 2.11:** The MEP, showing the electron density map with Color scales.

(d) Frontier Molecular Orbital (FMO)
The energy values of Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very useful quantum chemical parameters. Many descriptors are obtained using HOMO-LUMO orbitals. These values offer the data to determine the molecular reactivity, absolute electronegativity, hardness, electron transport and qualitative estimation of the excitation properties (Fukui K., 1982). The shapes of isodensity surface plots of HOMO and LUMO for the molecules are displayed by two distinct colors for positive and negative phases. The global hardness (\( \eta \)) of a molecule can be defined by the formula (Fukui K., 1982).

\[
\eta = \left[ -\varepsilon_{HOMO} + \varepsilon_{LUMO} \right] / 2 
\]

(2.22)

In same fashion, the absolute electro negativity is expressed as:

\[
\chi = \left[ \varepsilon_{HOMO} + \varepsilon_{LUMO} \right] / 2 
\]

(2.23)

Where \( \varepsilon_{HOMO} \) and \( \varepsilon_{LUMO} \) are the energy values of the HOMO and LUMO molecular orbitals. The softness is obtained by the taking inverse of hardness. The soft molecular systems are highly reactive and, high polarisable than the hard ones because small energy gap.

The electronic chemical potential (\( \mu \)) which measures the sensitiveness of the system’s energy to a change in number of electrons at fixed external potential (\( \mu = \left( \frac{\partial E}{\partial N} \right)_{\nu(F)} \)). The global hardness (\( \eta \)) which is the resistance of the electronic chemical potential to changes in the number
of electrons \( \eta = \left( \frac{\partial^2 E}{\partial N^2} \right) \frac{\nu(\vec{r})}{\nu(\vec{r})} = \left( \frac{\partial \mu}{\partial N} \right) \frac{\nu(\vec{r})}{\nu(\vec{r})} \) [Parr and Pearson (1983)] can be regarded as a resistance to charge transfer, whereas global softness \( (S) \) which is the inverse of the global hardness \( (S = \frac{1}{\eta} = \left( \frac{\partial N}{\partial \mu} \right) \frac{\nu(\vec{r})}{\nu(\vec{r})} \) [Yang and Parr (1985)], is a measure of the ease of charge transfer and is associated with high polarizability. Moreover, the electrophilicity index \( (\omega = -\Delta E \equiv \frac{\mu^2}{2\eta}) \), which measures the electrophilic power of a system [Chattaraj et al. (2006)], and which can be described as the maximum ability of a molecule to accept electrons in the neighborhood of an electron reservoir.

(e) Frequency:
Frequency calculation is one of the most crucial aspect for the quantum chemical calculations. This confirms the true minimum if there is no negative frequency. Calculation of frequency provides the large number of molecular parameters e.g. polarizabilities, free energies, enthalpy, rate of reaction and the IR/Raman spectra which are extremely useful information. The IR spectra can also be obtained in excited state using TDDFT methods which give the important structural information regarding the molecular system.

2.3.5 Electronic spectra:
Gaussian 09 bids many proficient methods to deal with the electronic spectroscopy of chemical systems (Barone, V. et al. 2009; Bloino, J., 2010). The energies for various electronic transitions, especially the absorption and emission, can easily be obtained using TD-DFT approach.

Usually, to obtain the intensity \( I \) of a particular electronic transition from state \( \Psi_m \) to \( \Psi_n \), we seek for the transition dipole moment because the intensity \( I \) of a transition is proportional to the square of transition dipole moment. The transition dipole moment is defined as:

\[
\mu_{nm} = \langle \Psi_n | \hat{\mu} | \Psi_m \rangle
\]  

(2.24)

where \( \hat{\mu} \) is the dipole operator, which can be written as

\[
\hat{\mu} = -e \sum_i r_i + e \sum_s Z_s R_s = \hat{\mu}_e + \hat{\mu}_N
\]  

(2.25)
Here $r_i$ and $R_S$ are the coordinates for electron and nucleon respectively and nuclear charges are represented by $Z_S$.

In general, the transition intensity (for one photon absorption or emission) can be defined as:

$$I = \alpha \beta \sum_m \sum_n \rho \gamma \delta \frac{(E_n - E_m)}{\hbar} - \omega$$  \hspace{1cm} (2.26)

Here the terms $I$, $\alpha$, $\beta$, $\gamma$, $d_{mn}^A$ and $d_{mn}^B$ have different values for different kind of spectroscopy, $\omega$ is the frequency of the emitted or absorbed photon, $\rho$ represents the Boltzmann population, $\delta$ is the Dirac function, and the double summation runs over all the energy states ($m$ for lower state and $n$ for higher ones).

In a first approximation level, electronic spectra absorption and emission spectra can be simulated by computing vertical excitation energies at geometrical structures optimized for the ground electronic state, with the resulting stick spectra subsequently convoluted by Gaussian or Lorentzian functions. However, such a treatment neglects completely dynamic effects, which influence significantly the spectrum line-shape in many cases. To overcome this limitation, a new procedure to compute vibrationally-resolved electronic spectra has been carried out by Gaussian 09 software. It relies on the Franck-Condon principle to evaluate the intensities of transitions between two vibronic states. This is done by considering that the nuclear positions are mostly unaltered by the electron jump which takes place during the electronic transition.

2.3.6 Vibrationally-Resolved Electronic (Vibronic) spectra:

Since vibronic transition take both the electronic and nuclear coordinate into account, if we consider an absorption transition, the initial state (ground state) can be represented as:

$$\mu_{\epsilon', \nu', \nu} = \langle \nu' (Q') | \mu_{\epsilon', \epsilon} (Q) | \nu (Q) \rangle$$  \hspace{1cm} (2.27)

Where $\nu (Q)$ and $\nu' (Q')$ are the functions for vibrations, $Q$ and $Q'$ are the normal modes belonging to ground and excited state respectively. The quantity $\mu_{\epsilon', \epsilon} (Q)$ denotes the electronic transition dipole moment. Since, there is no analytical expression in general for $\mu_{\epsilon', \epsilon} (Q)$, it is expanded in a Taylor series around the equilibrium geometry $Q_0$ as:
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\[ \mu_{e',e}(Q) = \mu_{e',e}(Q_0) + \sum_i \frac{\partial \mu_{e',e}}{\partial Q_i}(Q_i, Q_{io}) + \ldots \]  
(2.28)

In case of strongly dipole allowed transition, the expansion can be truncated under Franck-Condon approximation. For the transition dipole moment

\[ \mu_{e',\nu',\nu,\nu_e}= \mu_{e',e}(Q_0)(\nu'(Q')|\nu(Q)) \]  
(2.29)

The truncation after the second term of the expansion yields the FC-HT (Franck-Condon & Herzberg Teller) approximation:

\[ \mu_{e',\nu',\nu,\nu_e}= \mu_{e',e}(Q_0)(\nu'(Q')|\nu(Q)) + \sum_i \frac{\partial \mu_{e',e}}{\partial Q_i}(\nu'(Q')(Q_i - Q_{io})|\nu(Q)) \]  
(2.30)

For dipole forbidden transition \( \langle \nu'(Q')|\nu(Q) \rangle \) vanishes and the expression thus obtained is called HT (Herzberg Teller) approximation:

\[ \mu_{e',\nu',\nu,\nu_e}= \sum_i \frac{\partial \mu_{e',e}}{\partial Q_i}(\nu'(Q')(Q_i - Q_{io})|\nu(Q)) \]  
(2.31)

The occurrence of simultaneous excitation in vibrational and electronic states results in the mixing of transition dipole moment. In general the normal modes of ground state and excited state are not identical, this is called Duschinsky effect. Therefore, taking into account the computational bundle, it is necessary to express the excited state normal modes in terms of ground state normal modes. This is done by using Duschinsky transformation:

\[ Q' = JQ + K \]  
(2.32)

Where \( Q' \) are the excited state normal modes, \( Q \) are the ground state normal modes, \( J \) is Duschinsky matrix and \( K \) is the shift vector. This Duschinsky effect has been found quite good approximation. When the molecule does not undergo a noticeable distortion during the transition. The rotation or Duschinsky matrix and shift vector are given by:

\[ J = (L')^{-1} L'' \]  
and \[ K = (L')^{-1} M^{1/2} \Delta X \]

where \( L' \) and \( L'' \) are the transformation matrices from mass-weighted Cartesian coordinates to normal coordinates, \( M \) is the diagonal matrix of atomic masses and \( \Delta X \) is a vector representing the shift of nuclear Cartesian coordinates between the initial and final states. The computational vibronic absorption and emission spectra generated from above approximation give
good correlation with experimental findings. The difference in successive vibronic peaks, in wavenumber (cm$^{-1}$) gives the mode of vibration coupled with electronic transition discussed detail in chapter 3.

(a) Vibronic Absorption Spectra:

It is of huge important to obtain the excitation energies of particular molecular system. Computationally, it is done by TD-DFT linear response method. This method provides the oscillator strength and the position of electronic states in absorption. In order to obtained vibronically resolved absorption spectra, one needs the computed normal modes of vibration for the molecule in ground state and as well as in excited state. Depending of oscillator strength the models Franck-condon (FC), Franck-Condon- Herzberg-Teller (FCHT) or simply Herzberg-Teller (HT) can be employed to obtain the vibronic absorption spectra (Franck, J. et al., 1926; Condon, E. U., 1926; Herzberg, G., Teller, E., 1933). For the intensity of an absorption transition, the terms $I, \alpha, \beta, \gamma, d^A_{mn}$ and $d^B_{mn}$ have following values in equation (2.26):

\[
l = \epsilon(\omega), \quad \alpha = \frac{10\pi N_A}{3\epsilon_0 \ln(10) \hbar c} \\
\beta = 1, \quad \gamma = m, \quad d^A_{mn} = d^B_{mn} = \mu_{mn}
\]

(b) Vibronic Emission Spectra:

Computational estimation of emission energy is a multistep process (Gaussian 09 software package manual, 2010). The energy of emission can be obtained from the difference of single point energy of relaxed first excited state to the corresponding non-equilibrium ground state. The vibronic shape of emission spectra can also be obtained in same fashion as that of absorption but for the emission process, only FC method is available in Gaussian 09. The transition intensity of emission, bears the variables values as given below in equation (2.26):

\[
l = I_{em}/N_n \quad \alpha = \frac{2N_A}{3\epsilon_0 c^3} \\
\beta = 4, \quad \gamma = n, \quad d^A_{mn} = d^B_{mn} = \mu_{mn}
\]
(c) Electronic Circular Dichroism (ECD):

In silico spectra enable us to have better understanding and hidden facts behind position and shape of any spectral band. For the ECD spectroscopy, the concerned variable of equation (2.26) have following values:

\[
I = \Delta \varepsilon(\omega) \alpha = \frac{40\pi N_A}{3\varepsilon_0 \ln(10)hc^2} \\
\beta = 1, \quad \gamma = m, \quad d^A_{mn} = \mu_{mn}, \quad d^B_{mn} = l(m_{mn})
\]

In above expressions, \(\varepsilon(\omega)\) is the molar absorption coefficient, \(\Delta \varepsilon(\omega)\) is the difference between molar absorption coefficients of left handed and right handed circularly polarized light. \(\frac{I_{em}}{N_n}\) is mole/sec emitted energy. Moreover, the terms \(d^A_{mn}\) and \(d^B_{mn}\) are the transition moments of \(d^A\) and \(d^B\) between the lower and higher electronic states.

The experimental and computational methodology discusses above are used in the forthcoming chapters.