Chapter 2

Experimental and Theoretical Methods
This chapter deals with the materials, methodologies and characterization techniques employed for the synthesis of various neat and encapsulated transition metal complexes. The various physicochemical and spectrochemical techniques viz. scanning electron microscope (SEM), EDX, X-ray diffraction (XRD), thermo gravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, UV-visible/ diffuse reflectance spectroscopy(UV-vis/DRS), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR) spectroscopy and cyclic voltammetry (CV) used for the characterization of the synthesized complexes are highlighted with necessary theoretical background. The details of the computational methodologies use to study the structure, electronic and reactivity of the intrazeolite complexes and the mechanism of the catalytic reaction are discussed along with a brief introduction to density functional theory (DFT).

2.1. Materials Used

Table 2.1. The chemicals used in this study along with the manufacturers are listed below

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Sodium Y zeolite (NaY zeolite)</td>
<td>High Tech India. Ltd. Bombay, India</td>
</tr>
<tr>
<td>ii) Ferrous Chloride, FeCl₂.2H₂O</td>
<td>E-Merck, India</td>
</tr>
<tr>
<td>iii) Zinc Chloride, ZnCl₂.2H₂O</td>
<td>do</td>
</tr>
<tr>
<td>iv) anhydrous CuCl₂</td>
<td>do</td>
</tr>
<tr>
<td>v) anhydrous Ferric Chloride, FeCl₃</td>
<td>Otto Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>vi) Salicylaldehyde and its derivatives</td>
<td>Alfa Aesar, India</td>
</tr>
<tr>
<td>vii) <em>Ortho</em>-phenylenediamine</td>
<td>CDH (Central Drug House)</td>
</tr>
<tr>
<td>viii) Ethylenediamine</td>
<td>Merck</td>
</tr>
<tr>
<td>ix) Lithium Chloride</td>
<td>RANKEM, India</td>
</tr>
<tr>
<td>x) Potassium Nitrate</td>
<td>do</td>
</tr>
<tr>
<td>xi) 2-naphthol (analytical grade (AR),</td>
<td>G.S Chemical Testing Lab &amp; Allied</td>
</tr>
<tr>
<td></td>
<td>Industries, Bombay</td>
</tr>
<tr>
<td>xii) Tetrabutyl Ammonium Phosphate (TBAP)</td>
<td>E-Merck</td>
</tr>
<tr>
<td>xiii) Cobalt Chloride Hexahydrate, CoCl₂.6H₂O, and</td>
<td>RANKEM, India</td>
</tr>
<tr>
<td>xiv) Nickel Chloride Hexahydrate, NiCl₂.6H₂O,</td>
<td>do</td>
</tr>
<tr>
<td>xv) Copper Chloride Dihydrate, CuCl₂.2H₂O</td>
<td>do</td>
</tr>
<tr>
<td>xvi) Phenol (analytical grade (AR),</td>
<td>G.S Chemical Testing Lab &amp; Allied</td>
</tr>
<tr>
<td></td>
<td>Industries, Bombay</td>
</tr>
<tr>
<td>xvii) Picolinic Acid</td>
<td>Sigma-Aldrich, India</td>
</tr>
<tr>
<td>xviii) Chiral 1,2 diamine</td>
<td>do</td>
</tr>
</tbody>
</table>
Besides these the solvents used are of analytical grade (AR) and HPLC grade.

2.2. Experimental Methods

2.2.1. Synthesis of N, N’-bis(salicylidene)ethylenediamine (Salen)

To a 40 mmol salicylaldehyde (4.17 ml), 20 mmol ethylenediamine (1.33 ml) is added under cold condition. A yellow crystalline product so obtained after few minutes is further recrystallized in toluene. The purity and structure of the compound is analyzed by NMR, FT-IR and UV-vis techniques.

2.2.2. Synthesis of N,N’-disalicylidene-1,2-phenylenediamine (Salophen)

To a well stirred solution of 10 mmol o-phenylenediamine (1.08 g) in ethanol, 20 mmol salicylaldehyde (2.1 ml) is added. The mixture is stirred under reflux at 50 °C for 2h. A yellowish orange crystalline product is obtained which is further recrystallized in toluene and analyzed by NMR, FT-IR and UV-vis techniques.

2.2.3. Synthesis of 2,2’-(1,2-Diphenylethane-1,2-diyl)Bis(Azan-1-yl-1-ylidene)

Bis(Mthan-1-yl-1-ylidene)diphenol (L1)

The ligand L1 is synthesized according to Scheme 2.1. In a typical procedure a solution of (1R, 2R)-(+)-1,2-Diphenylethlenediamine (424mg, 2 mmol) and 2-hydroxybenzaldehyde (488mg, 0.426mL, 4mmol) in EtOH are stirred at room temperature for 18 h under nitrogen atmosphere. After completion of reaction, the reaction mixture is diluted with EtOAc and water. The organic layer is then separated and washed sequentially with brine and dried over Na₂SO₄. The solvent is removed in vacuum and the resulting residue is purified by chromatography. TLC is performed in 10% EtOAc and Hexane. The title compound is eluted at 6% EtOAc in Hexane. \( R_f = 0.4. \)

2.2.4. Synthesis of 6,6’-(1,2-Diphenylethane-1,2-diyl)Bis(Azan-1-yl-ylidene)

Bis(Methan-1-yl-1-ylidene)Bis(3-Methoxyphenol) (L2)

A solution of (1R,2R)-(+)-1,2-diphenylethylene- diamine (424mg, 2mmol) and 2-hydroxy-4-methoxy benzaldehyde (608mg, 4mmol) in EtOH is stirred at room temperature for 18 h under nitrogen atmosphere. After completion of reaction the reaction mixture is diluted with EtOAc and water. The organic layer is then separated and washed sequentially with brine and dried over Na₂SO₄. The solvent is removed in
vacuum and the resulting residue is purified by chromatography. TLC is run in 10% EtOAc and Hexane. The title compound is eluted at 6% EtOAc in Hexane. \( R_f = 0.4 \).

![Scheme 2.1. Synthesis of Chiral Schiff base Ligand L1 and L2](image)

### 2.2.5. Preparation of the Tris (1, 10 phenanthroline) M (II) complex, where \( M = \text{Fe, Cu and Zn}, [M(C_{12}H_{8}N_{2})_{3}]Cl_{2}.2H_{2}O \) (M-Phen or \( [M(Phen)]^{2+} \))

To a well stirred solution of 1,10 phenanthroline (0.595g, 3 mmol) in methanol (10ml) taken in a round bottom flask (50ml), a solution of FeCl\(_2.2H_2O\) (1mmol, 0.162g) in methanol (5 ml) is added. The resulting homogeneous solution is stirred at room temperature for 4 h. The solution is filtered and the filtrate on standing led to crystallization of the product. The black crystal so obtained is washed with ethanol followed by diethyl ether and dried at room temperature. The light greenish-blue crystal of copper and dirty white crystal of zinc are obtained following the same procedure using 0.135g (1mmol) anhydrous CuCl\(_2\) and 0.136g (1mmol) ZnCl\(_2.2H_2O\) in case of copper and zinc complexes, respectively in methanol.

### 2.2.6. Synthesis of Fe (III) Salen complex

To a well stirred solution of 1 mmol of \( N,N´\)-bis(salicylidene)ethylenediamine (0.268 g) in DMF (dimethylformamide), 1 mmol of anhydrous FeCl\(_3\) (0.162 g) is added. The homogeneous solution is stirred for 6 h and kept for crystallization. The black crystal so obtained is washed with ethanol and diethyl ether and finally dried at room temperature.
2.2.7. **Synthesis of Fe (III) Salophen complex**

Same procedure is carried out for the synthesis of this complex. The only difference is in the use of the ligand $N,N'$-disalicylidene-1, 2-phenylenediamine instead of $N, N'$-bis(salicylidene)ethylenediamine.

2.2.8. **Synthesis of Bis(Picolinato) M(II) [M= Co, Ni and Cu] complexes**

The bis(Picolinato) complexes $[\text{M}^{II}(\text{Pic})_2]$ are prepared according to the reported procedure.\(^{13}\) An aqueous solution of the free ligand is prepared by dissolving the free acid (picolonic acid) in a slight excess of dilute sodium hydroxide solution and adjusting the pH to 6-7 with dilute acid. The filtered ligand solution is then added to an aqueous solution of MCl$_2$.xH$_2$O in a 2: 1 ligand-metal mole ratio. The dark green compound is washed with acetone, ethanol and finally dried in vacuum. The purple and sky-blue complexes of cobalt and nickel, respectively are prepared using the same procedure.

2.2.9. **Preparation of Cu(L1)$_2$ and Cu(L2)$_2$ complex**

To a well stirred solution in acetonitrile (10 ml) taken in a round bottom flask (50 ml), a solution of the corresponding ligand (L1 or L2) dissolve in minimum volume of acetonitrile is added and stirred for 3h at 4°C. The resultant solution after three days gives greenish violet powders which are soluble in water.

2.2.10. **Preparation of alkali metal exchanged zeolites**

For the preparation of the alkali exchanged zeolite the NaY zeolite is used as precursor. The Na form of zeolite Y is treated with aqueous 1M NaCl solution once again and subsequently washed with distilled water until the silver ion test for chloride is negative. A mixture of 2.0 g NaY and 1 mmol (0.423 g) LiCl in demineralized water is then stirred under reflux at 120°C for 24h. The slurry is then filtered and washed with distilled water and dried overnight in oven to get Li-exchanged zeolite (Li-Y). The K-Y is obtained by exchanging NaY with 1 mmol (0.101 g) of KNO$_3$.

2.2.11. **Preparation of Fe (III) exchanged zeolites**

A mixture of 1 g of the alkali metal exchanged zeolites (LiY, NaY and KY) and 1 mmol (0.162 g) of anhydrous FeCl$_3$ solution in water are stirred under reflux at 120°C for 24h. The pH of the solution is maintained within 3-3.5 using buffer tablets order to prevent the precipitation ferric ion as Fe(OH)$_3$. The slurry is then filtered and washed
with distilled water and dried overnight in an oven at 500-550 °C to get Fe-exchanged LiY, NaY and KY as pale brown powders.

2.2.12. Preparation of metal exchanged zeolites $M^{2+}$ ($M = \text{Fe, Co, Ni, Cu, Zn}$) and Encapsulated Complexes

The various encapsulated transition metal complexes are synthesized following the general “flexible ligand” and ship in a bottle synthesis, shown in Table 2. The transition metal exchanged zeolites (Fe$^{2+}$-Y, Co$^{2+}$-Y, Ni$^{2+}$-Y, Cu$^{2+}$-Y and Zn$^{2+}$-Y) are first prepared by stirring a mixture of NaY (2.0g) and 1 mmol of individual metal chlorides [FeCl$_2$.2H$_2$O = 0.162g, CoCl$_2$.6H$_2$O = 0.237g, NiCl$_2$.6H$_2$O = 0.237g, CuCl$_2$.2H$_2$O = 0.170g and ZnCl$_2$.2H$_2$O = 0.136g] in 50 ml of water at 220 °C for 24h under refluxing condition. The pH of the solutions are maintained within 3-5 using buffer tablets in order to prevent the precipitation of metal hydroxides. The mixtures so obtained are washed with deionized water until the filtrate gives no white precipitate with AgNO$_3$ solution. Except Cu(II) Schiff base complexes all other encapsulated complexes are prepared via flexible ligand method. In a general flexible ligand method, the metal exchanged zeolites, dried at 500-550 °C are then treated individually with stoichiometric excess of the respective ligands to get zeolite encapsulated transition metal complexes. The powders obtained after 48 hours of stirring the mixtures in

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Representation</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Tris(1,10-Phenanthroline) complexes of Fe(II), Cu(II) and Zn(II)</td>
<td>Fe-PhenY/[Fe(Phen)$_3$-Y]$^{2+}$, Cu-PhenY/[Cu(Phen)$_3$-Y]$^{2+}$, Zn-PhenY/[Zn(Phen)$_3$-Y]$^{2+}$</td>
<td>dark brown, light greenish, pale white</td>
</tr>
<tr>
<td>iii) Picolinato Complexes of Co(II), Ni(II) and Cu(II)</td>
<td>[Co(Pic)$_2$]Y, [Ni(Pic)$_2$]Y, [Cu(Pic)$_2$]Y</td>
<td>dark brown, sky blue, blue-violet</td>
</tr>
<tr>
<td>iv) Chiral Schiff Base complex of Cu(II)</td>
<td>Cu(L1)$_2$-Y, Cu(L2)$_2$-Y</td>
<td>dark greenish</td>
</tr>
</tbody>
</table>
water-methanol solution refluxing at 220 °C are subjected to Soxhlet extraction for several hours using methanol and diethyl ether as solvents. The powders are then dried under vacuum and kept for 32h in a muffle furnace at 100 °C for further characterization.

The encapsulated transition metal complexes of copper here represented as Cu(L$_1$)$_2$-Y and Cu(L$_2$)$_2$-Y are synthesized following the general “Ship in a bottle ” synthesis method, Scheme 2.2. The copper exchanged zeolite is first prepared by stirring a mixture of NaY (2.0g) and 0.01mmol of anhydrous CuCl$_2$ in 50 ml of water at 220 °C for 24h under refluxing condition. The pH of the solutions is maintained within 3-5 using buffer tablets in order to prevent the precipitation of metal hydroxides. The mixture so obtained is washed with deionized water until the filtrate gives no white precipitate with AgNO$_3$ solution. The copper exchanged zeolite is then dried at 500-550 °C. To the copper exchanged zeolite, (1R,2R)-(−)1,2-diphenylethylene-diamine and 2-hydroxybenzaldehyde or its derivative dissolved in EtOH is added in stoichiometric amount and reflux at 40 °C fo 18h. The dark greenish powders obtained after 18 hours of stirring the mixtures are subjected to Soxhlet extraction for several hours using acetonitrile, ethanol and diethyl ether as solvents. The color of the samples remained same after Soxhlet extraction indicating the formation of metal complexes inside zeolite-Y. The powders are then dried under vacuum and kept for 32h in a desicator for further characterization.

\[
\text{Cu}^{2+} + 2\text{Ph}_2\text{C} = \text{CH}_2 + \text{OH} \rightarrow \text{Cu}^{2+}\text{-L}
\]

\[
\text{Cu}^{2+}\text{-Y} + \text{EtOH} \rightarrow \text{Cu}^{2+}\text{-L}_2\text{-Y}
\]

Scheme 2.2. Ship in a bottle synthesis of Cu-Schiff-base complex.
2.2.13. Catalytic Oxidation of 2-naphthol

The oxidation of 2-naphthol with air is carried out in a batch reactor. In a typical run, 5 mmol of 2-naphthol along with 10 ml of toluene, 10 mg of catalyst is added into a 100 ml two-necked flask equipped with a condenser and an air pump. The reaction is started by bubbling the dry air with a stable flow rate of 80 ml/min controlled by a flowmeter into the bottom of reactor at reaction temperature. The progress of the reaction is monitored by thin layer chromatography and after the completion of the reaction; the catalyst is filtered, washed with toluene and dried at 100 °C overnight. The amount of iron content in 10 mg of the catalyst is determined according to Vogels method. The turn over number is determined by following the equation, TON = [BINOL (mmol)/ Fe-atoms on catalyst (mmol)].

2.2.14. Catalytic Oxidation of Phenol

To a carry out the catalytic oxidation of phenol, the catalyst (15mg) is first treated with stoichiometric amount of 30% H$_2$O$_2$ and stirred for 10 min in nitrogen atmosphere. To this a solution of stoichiometric amount of phenol prepared in acetonitrile is added and the whole reaction mixture is subjected to microwave irradiation (280 watt). The progress of the reaction is monitored by TLC and UV-vis spectroscopy after an interval of 10 min. The solid catalyst is extracted by filtration and crude reaction mixture is quenched with saturated aqueous NH$_4$Cl and extracted with diethyl ether (3-20 mL), and the combined organic phases are dried over Na$_2$SO$_4$. A sample is taken for HPLC analysis, and the remaining mixture is evaporated and purified by column chromatography (EtOAc/petroleum ether 1:3) to afford catechol.

2.2.15. General Procedure for Asymmetric Henry Reaction

Asymmetric nitroaldol reactions are carried out in magnetically stirred glass reactor. Neat, Zeolite encapsulated chiral copper (II) complexes and Cu-exchanged zeoliteY(10mg) in either case is taken in ethanol (1 ml) and the resulting slurry is cooled to 0 °C. To the cold slurry, an appropriate aldehyde (1 mmol) is added with stirring and after a lag of 15 min; nitromethane (0.6 ml) is added through a syringe. The resulting suspension is stirred for 30 h at 0 °C. Reactions are monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. After completion of the reaction, the reaction mixture is purified by column chromatography on silica-gel column (20% ethyl acetate in n-hexane) to give the desired nitro-aldol adduct.
Enantiomeric excesses are determined by HPLC analysis using chiral columns (φ 4.6 mm × 250 mm, DAICEL CHIRALCEL OD-H or CHIRALPAK AD-H). NMR spectra are recorded on JEOL spectrometers in CDCl₃.

2.3. Methods of Characterization

2.3.1. X-ray Diffraction (XRD)

Powder X-ray diffraction (XRD) patterns are recorded on a Shimadzu XD-D1 powder X-ray diffractometer using Cu Kα radiation (λ = 1.542 Å). XRD patterns are recorded in the 2θ range of 5-50° at a scanning rate of 2°/min.

2.3.2. Fourier Transform Infra Red (FTIR) Spectroscopy

The infrared spectra in the range of 450-4000 cm⁻¹ are recorded on a Perkin-Elmer Spectrum 2000 FTIR spectrometer using a DRIFT accessory. The spectra of the neat and the zeolite-encapsulated complexes are recorded as KBr pellets by mixing the samples well with KBr.

2.3.3. Scanning Electron Microscopy (SEM)

The scanning electron microscope is often the preferred starting tool for analytic microscopy as it can provide a wide range of information. In SEM, a focused beam of high-energy electrons is scanned over the surface of a material. The electron beam interacts with the material, causing a variety of signals; secondary electrons, backscattered electrons, X-rays, photons, etc. each of which may be used to characterize a material with respect to specific properties. To study the surface topography and to assess the presence various elements, the SEM and elemental chemical analyses are performed by using JEOL JSM-6390 LV at an acceleration voltage of 5-15 kV. The samples are deposited on a brass holder and sputtered with platinum.

2.3.4. Ultra Violet visible/ Diffuse Reflectance Spectroscopy (UV-vis/DRS)

The absorption bands occurring in the visible and near-UV regions are used to obtain information on the electronic structure of catalyst. Most heterogeneous catalysts are opaque powdered samples from which light is reflected and not transmitted. The radiation reflected from a powdered crystalline surface consists of two specular component that is reflected from the surface without transmission (mirror reflection) and the diffuse component that is absorbed into the material and reappears at the surface after multiple scattering.
Chapter 2

The electronic absorption spectra are recorded using a Hitachi U-3400 spectrophotometer with a diffuse reflectance attachment equipped with an integrating sphere of 60 mm inner diameter. Mono-chromatic light was used in the whole spectral region in order to minimize the effect of fluorescence. The UV-vis spectra of the neat complexes and the ligands are recorded in solution mode and those of the metal exchanged zeolites and zeolite encapsulated metal complexes are recorded as the powdered samples. For recording absorption spectra of the powdered samples, the samples are placed in a black absorbing hole (10mm, in diameter and 3 mm deep) of a sample holder, and the surface is smoothen. The layer can be regarded as infinitely thick, as required by the Kubelka-Munk theory. The optical spectra are then recorded in the reflectance mode. A Kubelka-Munk (KM) analysis\(^2\) is performed on the reflectance data. The KM factor, \(F(R)\), is given by \(F(R) = (1-R)^2/2R = k/s\) where R is the diffuse reflectance of the sample as compared to BaSO\(_4\), \(k\) is the molar absorption coefficient, and \(s\) is the scattering coefficient of the sample.

2.3.5. **Electron Spin Resonance (ESR) Spectroscopy**

ESR spectra of neat complexes are recorded in appropriate solvents with Varian E–112 spectrometer at liquid nitrogen temperature (77 K). For encapsulated systems, the spectra are taken in solid state by taking 50 mg of the sample in a quartz tube.

2.3.6. **Cyclic Voltammetry**

The cyclic voltammograms of neat and encapsulated complexes are recorded on a Wenking potentioscan (model POS73) with a digital recorder, and 0.1 M TBAP is used as the supporting electrolyte. The working electrode is prepared by taking a 1:1 weight ratio of neat or encapsulated metal complexes in 1 ml of DCM. This suspension is ultrasonicated for 15 min. 10μL of this dispersion is coated on glassy carbon electrode and 5 μL of 5% styrene (as binder from Aldrich) is added on these coating and dried. The glassy carbon electrode is used as the working electrode and Ag/AgCl/KCl (saturated) is used as reference electrode. The cyclic voltammogram of neat complex is taken in solution mode, using 0.01M of the metal complexes in a 0.1M tetra butyl ammonium phosphate (TBAP). Cyclic voltammograms of all the catalysts are taken in 10 ml of DCM using 0.1M TBAP as supporting electrolyte.
2.3.7. Thermogravimetric Analysis (TGA)

Thermo-gravimetric and differential thermal analysis are performed on simultaneous TG-DTA thermo analyzer, Mettler Toledo, with a Pt crucible, Pt/Pt-Rh 13% thermocouples and flow rate of the controlling gas (air) of 20 mL/min.

2.3.8. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a well-known surface analytical technique widely used for investigating the chemical composition of solid surfaces with its attenuation depth of 20 Å. XPS is accompanied by irradiating a sample with monoenergetic soft X-rays and energy analysing the electrons emitted. Mg Kα (1253.6 eV) or Al Kα (1486.6 eV) X-rays are ordinarily used. These photons have limited penetrating power in a solid, of the order of 1-10 micrometers. They interact with atoms in this surface region by the photoelectric effect, causing electrons to be emitted. The emitted electrons have kinetic energy (KE) given by

\[ KE = h\nu - BE - \phi_s \]

where, \( h\nu \) is the energy of photon, \( BE \) is the binding energy of atomic orbital from which the electron originates, \( \phi_s \) is the spectrometer work function.

The binding energy may be regarded as ionization energy of the atom for the particular shell involved. Since there are a variety of possible ions from each type of atom, there is a corresponding variety of kinetic energies of the emitted electrons.

The XP spectra of neat and encapsulated picolinato complexes and metal exchanged zeolites viz, Cu\(^{2+}\)Y, Co\(^{2+}\)Y and Ni\(^{2+}\)Y are made on a KRATOS (ESCA AXIS 165) spectrometer by using Mg Kα (1253.6 eV) radiation as the excitation source. Charging of catalyst samples are corrected by setting the binding energy of the adventitious carbon (C\(_{1s}\)) at 284.6 eV. The finely ground oven-dried samples are dusted on a double stick graphite sheet and mounted on the standard sample holder. The sample holder is then transferred to the analysis chamber, which can house 10 samples at a time, through a rod attached to it. The samples are out gassed in a vacuum oven overnight before XPS measurements.

2.4. Density Functional Theory (DFT) Calculation

Density functional theory (DFT) calculations are performed on the neat and the zeolite Y encapsulated complexes to understand the effect of zeolite matrix on the structure, electronic and reactivity of the transition metal complexes. Further, DFT
calculations are also performed to study mechanism of phenol oxidation by metal picolinato complexes and the Henry reaction catalysed by chiral Cu-Schiff base complexes. So herein we provide a brief account of density functional theory before describing the methodologies employed for such calculations.

2.4.1. Density Functional Theory

The ground state energy of a collection of atoms may be computed by solving the Schrödinger equation – the time independent and non relativistic form of which is given by,

\[ \hat{H} \psi (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E \psi (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \]  

(1)

The Hamiltonian operator, \( \hat{H} \), is the summation of kinetic energy, the interaction with the external potential (\( V_{\text{ext}} \)) and the electron-electron interaction (\( V_{\text{ee}} \)), i.e.,

\[ \hat{H} = -\frac{1}{2} \sum_i^{N} \nabla_i^2 + V_{\text{ee}} + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \]

(2)

In general, the external potential of interest is simply the interactions of electrons with the atomic nuclei;

\[ V_{\text{ext}} = -\sum_{\alpha}^{N_{\text{at}}} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \]

(3)

where \( \mathbf{r}_i \) and \( \mathbf{R}_\alpha \) are the coordinate of electron \( i \) and nucleus \( \alpha \) respectively, and \( Z_\alpha \) is the charge on the nucleus. For simplification, the spin part is omitted here and from further discussions on DFT. Equation 1 is solved for a set of \( \psi \) with the antisymmetric constraint. The lowest eigenvalue, \( E_0 \), is the ground state energy and the probability density of finding an electron with any particular set of coordinates \( \{\mathbf{r}_i\} \) is \( |\psi_0|^2 \). The average value of a state for a particular \( \psi \) is the expectation value of \( \hat{H} \), i.e.,

\[ E[\psi] = \int \psi^* \hat{H} \psi \, d\mathbf{r} \equiv \langle \psi | \hat{H} | \psi \rangle \]

(4)

The notation \( E[\psi] \) indicates that energy is a functional of the wavefunction. The variational theorem states that the energy so obtained is higher than that of the ground state energy (\( E_0 \)) unless \( \psi \) corresponds to \( \psi_0 \).

\[ E[\psi] \geq E_0 \]

(5)

The ground state wavefunction and the energy may be evaluated by looking for all possible wavefunctions and finding the one that minimizes the total energy. One such procedure is Hartree-Fock theory where the total wavefunction is assumed to be the antisymmetric product of functions (\( \varphi_i \)) each of which is dependent on the coordinates of one electron, i.e.,
\[ \psi_{HF} = \frac{1}{\sqrt{N!}} \text{det} [\phi_1 \phi_2 \phi_3 \ldots \phi_N] \]  

where ‘det’ indicates a matrix determinant. Substitution of \( \psi \) into Schrödinger equation results in Hartree-Fock expression for energy;

\[ E_{HF} = \int \varphi_i^*(r) \left( -\frac{1}{2} \sum_{l} \nabla_l^2 + V_{ext} \right) \varphi_i (r) dr \]

\[ + \frac{1}{2} \sum_{i,j}^{N} \int \varphi_i^*(r_1) \varphi_i(r_1) \varphi_j^*(r_2) \varphi_j(r_2) \frac{1}{|r_i - r_j|} dr_1 dr_2 \]

\[ - \frac{1}{2} \sum_{i,j}^{N} \int \varphi_i^*(r_1) \varphi_j(r_1) \varphi_i(r_2) \varphi_j^*(r_2) \frac{1}{|r_i - r_j|} dr_1 dr_2 \]

The second term in eqn. 7 is the classical coulomb energy and the third term is the exchange energy written in terms of the orbitals. Applying variation theorem to the energy expression within the constraint that orbitals are orthonormal yields the ground state energy and lead to the Hartree-Fock equations,

\[ [-\frac{1}{2} \nabla^2 + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} dr'] \varphi_i(r) + \int V_X(r, r') \varphi_i(r') dr' = \varepsilon_i \varphi_i(r) \]  

where \( V_X \) is the non-local exchange potential and is such that

\[ \int V_X(r, r') \varphi_i(r') dr' = -\sum_j^N \int \frac{\varphi_j(r) \varphi_j^*(r')}{|r-r'|} \varphi_i(r') dr' \]

Thus, the Hartree-Fock equations describe non-interacting electrons under the influence of a mean potential field consisting of the classical coulomb potential and a non-local exchange potential. From this point onwards, better approximation (correlated methods) for \( \psi \) and \( E_0 \) are readily obtained. However, the cost of such computation is very high. Many correlated methods are now available such as MP2, MP3, MP4, CISD, CCSD and CCSD(T) which formally scales with the number of electrons raised to the power of 5,6,7,6,6 and 7, respectively. In most cases, the accuracy of CCSD(T) calculations are sufficient enough for determination of chemical properties. However, the accuracy of such calculations comes at very high cost thereby limiting their use in real systems. Thus, it appears that solution of Schrödinger’s equations for realistic system is very cumbersome. This gave rise to the development of a new theory called the density functional theory.
The Hamiltonian operator (eqn. 2) involves the coordinates of one and two electrons only. For the computation of total energy, knowledge of two-particle probability density, i.e., probability of finding an electron at \( \mathbf{r}_1 \) and another at \( \mathbf{r}_2 \) is sufficient. This implies that the total energy can be computed without the proper knowledge of 3N dimensional wave function.

The second order density matrix, a quantity of great use in analyzing the energy expression, is given by,

\[
P_2(r_1, r_2; r_1', r_2') = \frac{N(N-1)}{2} \int \psi^*(r_1', r_2', ..., r_N') \psi(r_1, r_2, ..., r_N) dr_3 dr_4 ... dr_N
\]  

The diagonal elements of \( P_2 \), referred to as two-particle density matrix or pair density, are given by,

\[
P_2(r_1, r_2) = P_2(r_1, r_2; r_1, r_2)
\]

This is the required two electron probability function which determines all two particle operators. The first order density matrix, \( P_1 \), may be defined in a similar way and can be written in terms of \( P_2 \) as,

\[
P_1(r_1', r_1) = \frac{2}{N-1} \int P_2(r_1', r_2'; r_1, r_2) dr_2
\]

Knowing \( P_1 \) and \( P_2 \), the total energy can be determined exactly,

\[
E = \int \left[ \left( -\frac{1}{2} \nabla^2 + \sum_{\alpha} \frac{Z_\alpha}{|r_1 - R_\alpha|} \right) P_1(r_1', r_1) \right] dr_1 + \int \frac{1}{|r_1 - r_2|} P_2(r_1, r_2) dr_1 dr_2
\]

The diagonal elements of the first and second order density matrices completely determine the total energy. This vastly simplifies the task. The solution of full Schrödinger equation for \( \psi \) is not required – it is sufficient to determine \( P_1 \) and \( P_2 \) – and the problem in 3N coordinates space has been reduced to a problem in a 6 dimensional space.

Direct minimization of \( E(P_1, P_2) \) suffers from specific problems as the density matrices should be constructed from an antisymmetric \( \psi \). This is non trivial and currently an unsolved problem.\(^4\) Thus, it appears that eqn. 12 does not lead immediately to a reliable method for computing the total energy without calculating the many body wavefunction. However, the fact that boosts the density functional theory is the diagonal elements of the first order density matrix, i.e., the charge density, can completely determine the ground state energy.
2.4.2. The Hohenburg-Kohn Theorems

In 1964, Hohenburg and Kohn provided two theorems\(^5\) which simplified the task in hand. The first theorem may be stated as:

*The electron density determines the external potential (to within an additive constant).*

As the external potential is used to specify the Hamiltonian operator (eqn. 2), thus, in principle, the Hamiltonian operator can be uniquely determined by the charge density and all the wavefunction of all the states can be computed. The second theorem establishes a variational theorem for a system of N electrons:

*For any positive definite trial density, \(\rho_t\), such that \(\int \rho_t(\mathbf{r}) \, d\mathbf{r} = N\), then \(E[\rho_t] \geq E_0\).*

The two theorems lead to the fundamental statement of density functional theory:

\[
\delta [E[\rho] - \mu(\int \rho(\mathbf{r}) d\mathbf{r} - N)] = 0
\]

(13)

where \(\mu\) is the chemical potential or the Lagrange multiplier of the constraint that the density contains the correct number of electrons. Thus, it appears that there is a *universal* functional \(E[\rho]\) (i.e., it is independent of the external potential) which, if we know its form, can be inserted into the above equation and minimized to obtain the exact ground state density and energy.

2.4.3. The Energy Functional

The energy functional contains three terms – the kinetic energy, the interaction with external potential and the electron-electron interaction;

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

The interaction with external potential is given by,

\[
V_{ext}[\rho] = \int \mathbf{V}_{ext} \rho(\mathbf{r}) d\mathbf{r}
\]

The kinetic and electron-electron functionals are not known. Direct minimization of the energy would be possible if good approximation to these functionals could be found. This possibility is a matter of recent research.\(^6\)

Kohn and Sham proposed the following for approximating the kinetic and electron-electron functionals.\(^7\) They introduced a system of N non-interacting electrons to be described by a single determinant wave function in N “orbitals” \(\phi_i\). In this system, the kinetic energy and electron density are known exactly from the orbitals,

\[
T_s[\rho] = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle
\]

The true ground state density can be expressed in terms of \(\phi_i\) as,
The construction of density from a set of orbitals ensures that it is legal and can be constructed from an asymmetric wavefunction.

If one considers that classical Coulomb interaction or the Hartree energy represents a significant component of electron-electron interaction, then the second term in eqn. 7 written in terms of density will be,

\[ V_H[\rho] = \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} d^3r_1 d^3r_2 \]

The energy functional can be rearranged as,

\[ E[\rho] = T[\rho] + V_{\text{ext}}[\rho] + V_H[\rho] + E_{xc}[\rho] \]

where \( E_{xc}[\rho] \) is the exchange-correlation functional which can be expressed as,

\[ E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - V_H[\rho]) \]

\( E_{xc} \) is simply the sum of error in using a non-interacting kinetic energy and the error in treating the electron-electron interaction classically. Writing the functional (eqn. 15) explicitly in terms of the density obtained from non-interacting orbitals (eqn. 14) and applying the variational theorem (eqn. 13), one finds that the orbitals which minimize the energy satisfy the following set of equations,

\[ \left[ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(r) + \frac{\rho(r)}{|r-r'|} + V_{xc}(r) \right] \phi_i(r) = \epsilon_i \phi_i(r) \]

where the local multiplicative potential is the functional derivative of exchange correlation energy with respect to the density,

\[ V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho} \]

This set of non-linear equations (the Kohn-Sham) describes the behavior of non-interacting electrons under the influence of an effective local potential. Thus, for the exact functional and exact local potential, the orbitals yield the exact ground state density and energy via eqn. 14 and 15, respectively. These Kohn-Sham equations are similar to the Hartree-Fock equations (eqn. 8) where the non-local exchange potential has been replaced by the local exchange-correlation potential, \( V_{xc} \). However, the exact functional and its associated potential are not known. But, in principle, it is possible to solve the Schrödinger equations for a particular system and determine the energy functional and its associated potential. This of course needs greater effort. Nevertheless, the ability to determine the universal functional in a number of systems
allows excellent approximations to the functional to be made. The approximations are
discussed below in brief.

For calculations in which energy is the quantity of primary interest, DFT
provides excellent and highly accurate alternative to the costly wavefunction based
methods. However, the utility of this theory (DFT) is dependent on the approximation
used for \( E_{xc}[\rho] \).

2.4.4. The Local Density Approximation for \( E_{xc}[\rho] \)

The generation of approximations for \( E_{xc} \) has initiated a rapidly expanding field
of research. Different functional are now available which are more or less appropriate
for any particular study. The early model that led to a practical utility of density
functional theory was that of homogeneous electron gas for which exact results could be
obtained. In this model, the electrons are subjected to a constant external potential and
hence, the charge density is constant. The system can be specified by a single number –
the value of the constant electron density, \( \rho = N/V \).

The homogeneous electron gas was studied by Thomas and Fermi in 1920’s considering
the plane wave orbitals of the system. If the electron-electron interaction is
approximated by classical Hartree potential (i.e., neglecting exchange and correlation
effects), then the total energy functional can be readily obtained. Under these
conditions, the kinetic and exchange energy (equation 7) can be expressed in terms of local
functions of density. Application of the kinetic and exchange energy densities of the
non-interacting homogeneous electron gas leads to following eqns,

\[
T[\rho] = 2.87 \int \rho^5(r)dr \quad \text{and}, \quad E_x[\rho] = 0.74 \int \rho^4(r)dr
\] (18)

The local exchange correlation energy per electron may be approximated as,

\[
E_{xc}[\rho] \approx \int \rho(r)\varepsilon_{xc}(\rho(r))dr
\] (19)

where \( \varepsilon_{xc}(\rho) \) is the local charge density which by choice is approximated to be the
exchange and correlation energy density of the homogeneous electron gas of density \( \rho \).
This is the local density approximation (LDA). Within LDA, \( \varepsilon_{xc}(\rho) \) can be separated
into exchange and correlation contributions,

\[
\varepsilon_{xc} = \varepsilon_x(\rho) + \varepsilon_c(\rho)
\] (20)

The Dirac form of \( \varepsilon_x \) can be written as,

\[
\varepsilon_x(\rho) = -C \rho^{1/3}
\] (21)
where \( C \) is a constant introduced rather than that determined for a homogeneous electron gas. The functional form of the correlation energy density \( \varepsilon_c(\rho) \) is unknown and can be obtained by numerical Monte Carlo calculations on homogeneous electron gas which yield exact results.\(^{10}\)

LDA has been a fruitful approximation by the fact that it reduces the energy functional to a simple local function of the density. It provides reliable results of many properties such as structure, vibrational frequencies etc. However, in computing energy difference between rather different structures, energy barriers in diffusion or chemical reactions, LDA has proven to be not so reliable. Thus, the modification of the approximation is required and as such is now available.

One of the obvious extensions of the LDA is to recognize that the exchange contribution to the energy is dominant over the correlation energy for many systems. Thus, computation of the non-local exchange potential exactly as in Hartree Fock theory (eqn 7) and approximating the correlation potential within the LDA would yield a functional of the form,

\[
E_{xc} \approx E_{Fock} + E_c^{LDA}
\]

2.4.5. The Generalized Gradient Approximation

The LDA can be considered as the zeroth order approximation to the semi-classical expansion of the density matrix in terms of the density and its derivative. A natural strategy is to adopt the gradient expansion approximation (GEA) in which the first order gradient terms in the expansion is included.

In the generalized gradient approximation (GGA), a functional form is implemented which ensures the normalization condition and leads to an energy functional that depends on both density and its gradient. However, the analytical properties of the exchange correlation hole within LDA are retained. The typical form for a GGA functional is,

\[
E_{xc} \approx \int \rho(\mathbf{r})\varepsilon_{xc}(\rho, \nabla \rho) d\mathbf{r}
\]

2.4.6. Meta-GGA Functionals

Recently, functionals that depend on the Laplacian of the spin density or of the local kinetic energy density have been developed.\(^{11}\) Such functionals are referred to as meta-GGA functionals.

The typical form of such a functional is,
where the kinetic energy density is

\[ \tau = \frac{1}{2} \sum_i |\nabla \varphi_i|^2 \]  

(25)

Significant advances in approximations for \( E_{xc}[\rho] \) have made DFT a practical, efficient and unbiased tool for computing various properties of molecules.

### 2.5. Theoretical Methods

All DFT calculations are carried out using the DMol\(^3\) program\(^{15}\) with VWN correlation functional and double numeric (DN) basis set. We performed all electron calculations for the neat phenanthroline complexes of iron, copper and zinc and for those encapsulated inside the framework of zeolite. The zeolite clusters generated by taking 40 tetrahedral units (40T) of faujasite structure around the supercage, saturating them with hydrogen atoms. Initially, the framework Si and O atoms of the clusters are held fixed at their crystallographic positions and all the terminal H atoms are optimized. Following Löwenstein’s rule depending on the overall charge of the complexes, silicon atoms of the six-member ring are replaced with aluminium atoms. For example in case of doubly charged complexes two silicon atoms are replaced by two aluminium atoms. The gas phase optimized complexes are then encapsulated inside the supercage at several orientations. The two negative charges generated in the cluster are compensated by two positive charges of the complexes. While optimizing the clusters, terminated hydrogen atoms are held fixed at their initially optimized positions.

Following the Koopmans theorem\(^{12}\), the chemical potential (\( \mu \)) and global hardness (\( \eta \)) can be expressed as

\[ \mu = \frac{E_{LUMO} + E_{HOMO}}{2} \]  

(26)

\[ \eta = \frac{E_{LUMO} - E_{HOMO}}{2} \]  

(27)

where, \( E_{LUMO} \) is the energy of the lowest unoccupied molecular orbital and \( E_{HOMO} \) is the energy of the highest occupied molecular orbital.

However, the finite difference approximation defines the above quantities in terms of ionization potential (IP) and electron affinity (EA) of the system\(^{13}\):

\[ \text{IP} = E_{N-1} - E_N \]  

(28)

\[ \text{EA} = E_N - E_{N+1} \]  

(29)
where $E_N$, $E_{N-1}$ and $E_{N+1}$ are energies of $N$, $N-1$ and $N+1$ electron system.

In most numerical applications, chemical potential ($\mu$) and chemical hardness ($\eta$) are calculated using finite difference approximation in terms of IP and EA and therefore, $\mu$ and $\eta$, given below, can be used as a working formula

$$\mu = -\frac{(IP + EA)}{2}$$  \hspace{1cm} (30)

$$\eta = \frac{(IP - EA)}{2}$$  \hspace{1cm} (31)

The global electrophilicity as introduced by Parr et al.\(^\text{14}\) can be defined as

$$\omega = \frac{\mu^2}{2\eta}$$  \hspace{1cm} (32)

The global softness $S$ is defined as the inverse of the global hardness $\eta$,

$$S = \frac{1}{2\eta}$$  \hspace{1cm} (33)

In a finite difference approximation, the condensed Fukui function\(^\text{15}\) of an atom, $k$, in a molecule with $N$ electron is defined as

$$f^+_{k} = [q_k (N+1) - q_k (N)]$$ (for nucleophilic attack)  \hspace{1cm} (34)

$$f^-_{k} = [q_k (N) - q_k (N-1)]$$ (for electrophilic attack)  \hspace{1cm} (35)

$$f^0_{k} = \frac{(q_k (N+1) - q_k (N-1))}{2}$$ (for radical attack)  \hspace{1cm} (36)

where $q_k (N)$, $q_k (N+1)$ and $q_k (N-1)$ are the charges of the $k^{th}$ atom for $N$, $N+1$ and $N-1$ electron systems, respectively.

The global reactivity descriptors, chemical potential, hardness, electrophilicity index and softness are calculated using equations (27)-(33), respectively. The Hirshfeld population analysis (HPA) is used to calculate the Fukui functions. The Fukui functions (FFs, $f^+_{k}$ and $f^-_{k}$) are calculated using equations (34) and (35).

TDDFT calculation have been performed in methanol solution using the B3LYP exchange correlations functional\(^\text{16}\) and 6-31G basis set\(^\text{17}\) as implemented in the Gaussian03 program package.\(^\text{18}\) Solvation effects are included by means of the conductor-like polarizable continuum model (C-PCM).\(^\text{19}\) In case of Fe(Phen)$_3^{2+}$ complex, 100 excitation energies and in case of Cu and Zn analogues 150 excitation energies are computed. The simulation of the absorption spectra are performed by a
convolution of Gaussian function centered at the calculated excitation energies for all excitation.

To study the cis-trans isomerization process and the mechanism of phenol oxidation. The PBE1 functional, is used (as provided in Gaussian 03 program) since it performs exceedingly well for the evaluation of energetics of a reaction as well as many other properties. The relativistic small-core effective core potential (ECP) of Stuttgart/Dresden (SDD) for the transition metals are used. As stated by Bühl et al, the combination of PBE1 and SDD can safely be used for studying transition metal complexes. Frequency calculations are performed at the same level of theory to characterize the nature of the stationary points. All the ground state structures are verified as being at an energy minimum by confirming that their respective Hessian (matrix of analytically determined second order derivative of energy) led to all real valued frequencies while the transition states are characterized as stationary points with one imaginary frequency.

References