INTRODUCTION:
1.1 Preamble:

The fundamental underpinnings of theoretical chemistry were uncovered at the beginning of the 20th century. Rutherford's discovery of the nucleus in 1911 completed the identification of the constituent sub-particles of atoms and molecules and was followed shortly thereafter by the Bohr treatment of electronic orbits in atoms. The relation between the positive nuclear charge, atomic number, and position of an atom in the periodic table was uncovered by 1913. Bohr's orbit theory can not be extended to polyatomic systems and the next advance had to await the development of the wave theory of matter and the associated quantum mechanics in the early 1920s. In 1926 Heisenberg developed new mechanics based on the matrix theoretic approach. Schrödinger independently proposed the basic nonrelativistic wave equation governing the motion of nuclei and electrons in molecules. The fundamental equation \( H\Psi = E\Psi \) is of a second order, first-degree differential equation and the wavefunction \( \Psi(r, t) \) predicts behavior of matter at the molecular (microscopic) level. A direct quantitative prediction of chemical properties of a system can be derived from the exact solution to the Schrödinger equation. For the systems having more than one electron, however, the exact solution of this equation can not be obtained. Good quality numerical solutions instead are achieved only after complex mathematical operations. Thus the practical applications of the Schrödinger equation seems to be restricted which necessities formulation of approximate methods for the many electron atomic or molecular systems. Advent of computers and the availability of a variety of software have made it possible to deal with the complex mathematical problems. Until the late 1970's, limitations of computer memory, hard disk storage and the CPU speed constituted a major bottleneck to explore
the applications of \textit{ab initio} (\textit{Latin: from the beginning or from the first principles}) electronic structure methods. In the recent years the advances in supercomputers, or the vector/parallel machines, powerful workstations and desktop computers have widened the scope for running the electronic structure programs for the systems upto nearly 100 atoms or so. With the aid of quantum chemical (QC) tools, one can predict not only the structure and charge distribution but also the accompanying properties related to the spectroscopy and thermodynamics. Thus a variety of properties encompassing the equilibrium molecular geometry, total energy, Frontier orbitals, electron affinity, multipole moments, polarizabilities, electronic, vibrational and rotational transitions, nuclear and electron-paramagnetic shielding constants \textit{etc} can be derived for the isolated molecules and small clusters as well.

In order to model the chemical properties one may employ different methods based on (a) Molecular mechanics (MM) (b) semi-empirical quantum chemical methods (c) \textit{ab-initio} quantum chemical methods (d) the density functional methods. On the other hand the molecular dynamics and Monte Carlo based methods can be explored to investigate the macroscopic properties of a system. The MM methods\textsuperscript{2-4} employ the treatment of classical mechanics, wherein the total energy is assumed to be function of nuclear coordinates solely, turns out to be the least expensive computational method, while it can handle chemical systems such as proteins, enzymes and other macromolecular systems, containing tens of thousands of atoms. However, there is a compromise in the accuracy of predicted results of such calculations, which are dependent on the force fields (FFs) used. On the other hand, \textit{ab initio} methods provide a mathematical description of the chemical system by solving the Schrödinger equation from first principles, without employing any
empirical data except the universal constants. Hence, the results obtained from these sophisticated \textit{ab initio} methods are known to be accurate and generally are in good agreement with the experimental results\textsuperscript{5}.

By far, the Hartree-Fock (HF) formulation that uses, in its simplest form, a single-determinantal form of wavefunction subjected to the variational principle as discussed later, is the most commonly used \textit{ab initio} method. It, however, should be remarked here that in the HF theory the correlation between electron pair with of opposite spins is not accounted. This necessitates the use of post-HF methods and bridge the gap between HF-level and electronic energies determined from the experiments. The methods like configuration interaction (CI) and coupled-cluster (CC) are some of the examples of such high-quality \textit{ab initio} methods, which provide accurate energies and molecular properties. Due to its high computational cost, these methods can be employed for systems with utmost a few tens of atoms. The second order correction term in the Møller-Plesset perturbation theory (MP2) has been widely recognized as an attractive post-HF alternative. The expensive computational requirements, however, restrict their use to only relatively small or medium-sized molecules. On the other hand for dealing with the large molecular systems different approximations and parameterizations schemes has led to a plethora of methods termed as the semi-empirical methods\textsuperscript{6, 7}. These semi-empirical methods have proved useful for the molecular systems containing a few thousands of atoms.

The Hohenberg-Kohn\textsuperscript{8} and Kohn-Sham\textsuperscript{9} formalisms proposed in 1964 and 1965 respectively, formally led another school of thinking, that the physical observables of a system in its ground state can be expressed as functionals of the electron density (ED). The density functional theory\textsuperscript{10} (DFT) has become quite successful and popular in the
recent times. DFT-based methods promise to provide reliable predictions of the structure and properties of chemical systems with lesser computational effort than that required for post-HF methods. The computational cost the HF and DFT level calculations on medium/large-sized molecules, practically scales as $O(N^3)$, $N$ being the number of basis functions used in the calculations. An outline of the molecular mechanics and the quantum chemical methods is presented below.

1.2 Molecular Mechanics Methods:

The molecular mechanics (MM) methods treat molecules as classical objects made of hard-sphere atoms and spring-like elastic bonds. The energies calculation and properties involve empirical parameters and employ classical equations of motion. A force constant obtained from existing empirical data or from accurate \textit{ab initio} treatment defines the behavior of bonds between specific pairs of atoms. Similarly, several empirical parameters are used to arrive at the energy of the system as contributions due to bonding, angular, torsion and van der Waals and electrostatic interactions as shown below.

$$E = E_{\text{bond}} + E_{\text{bend}} + E_{\text{torsion}} + E_{\text{vdW}} + E_{\text{electrostatics}} + \ldots$$  (1.1)

There are several sets of force fields (FF) that define these parameters for a given atom and atom-pair. The MM method does not treat electrons explicitly and the FF implicitly includes the electronic contributions. The MM method is an inexpensive computational method and hence can be used to study chemical systems with several thousands of atoms. However, there is a compromise in the accuracy of results from such calculations, which are solely dependent on the FFs used. Reliable energies can be only
obtained by using extensive parameterization over a class of compounds. The currently popular FFs include AMBER\textsuperscript{12}, OPLS\textsuperscript{13}, CHARMm\textsuperscript{14} (both suited for studying biological systems), MMFF\textsuperscript{15}, Dreiding\textsuperscript{16}, UFF\textsuperscript{17} etc. The FFs are obtained by fitting the experimental or \textit{ab initio} results and hence suffer from transferability to other systems. Further, MM methods cannot be employed to investigate chemical problems where electronic effects dominate.

1.3 Quantum Chemical Methods:
In all these methods, the electronic structure of matter is described in terms of Schrödinger equation. The term \textit{ab-initio} simply suggest that the chemical phenomenon are explained in terms of fundamental physical constants such as Planck’s constant, velocity of light, mass of electrons and nuclei. Other than the determination of these constants, \textit{ab-initio} methods are independent of experiments. Since most of the chemical phenomena are due to the time-dependent interactions, one may write time-independent Schrödinger equation, which written in its simplest form is

$$\mathbf{H}\Psi = E\Psi$$

(1.2)

where $\mathbf{H}$ is the Hamiltonian operator comprising of the nuclear and electronic kinetic energy operators and the potential energy operators corresponding to the nuclear-nuclear, nuclear-electron and electron-electron interactions. The many-particle wavefunction $\Psi$ describes the system, while $E$ is the energy eigenvalue of the system.

In 1927, Born and Oppenheimer (BO) proposed an approximation\textsuperscript{18} that led to a major leap towards a practical solution to the Schrödinger equation. The BO approximation is based on the notion that the nuclear and electronic motions take place at different time scales, the latter being much smaller than the former. Hence, an electron in
motion sees relatively static nuclei, while a moving nucleus feels averaged electronic motion. It has been found that the calculations beyond BO approximation lead to an error of approximately 0.3%. Thus this enables one to separate the electronic and nuclear Hamiltonians and the corresponding wavefunctions as well. The molecular wavefunction can then be represented as a product of electronic and nuclear counterparts.

\[ \Psi(\{r_i\};\{R_A\}) = \Phi_{\text{elec}}(\{r_i\};\{R_A\})\Phi_{\text{nuc}}(\{R_A\}) \]  

Here, \( \{r_i\} \) and \( \{R_A\} \) are the positions of electrons and nuclei, respectively. The eigenvalue equation for the electronic case is then written as

\[ \mathbf{H}_{\text{elec}} \Phi_{\text{elec}}(\{r_i\};\{R_A\}) = E_{\text{elec}} \Phi_{\text{elec}}(\{r_i\};\{R_A\}) \]  

The electronic Hamiltonian depends explicitly on the electronic coordinates and parametrically on nuclear coordinates. Since the chemical phenomena occur primarily due to various interactions between electrons of the systems, explicit treatment of the electronic Hamiltonian generally suffices to investigate chemical properties and reactions. However, probing the vibrational, rotational and translational motions of molecules would further require an explicit treatment using the nuclear Hamiltonian.

The system of atomic units (a.u.), sometimes referred as Hartree units, has been conveniently adopted as a convention in QM wherein the mass of an electron, Planck's constant, charge of a proton, the length corresponding to radius of first Bohr orbit in hydrogen atom and \( 4\pi \) times the permittivity in free space (\( 4\pi\varepsilon_0 \)) are all set to unity and the unit of energy in a.u. numerically turns out to be one-half the energy of a hydrogen atom in its ground state (GS). The use of atomic units leads to a simplified and convenient electronic Hamiltonian (excluding the internuclear repulsion) as shown below.
The first term is the electronic kinetic energy operator summed over the number of electrons, $N$. The second term represents coulombic attraction between electrons $\{i\}$ and $M$ nuclei $\{\Lambda\}$, while $\{Z_A\}$ are the nuclear charges. The last term attributes to the Coulombic repulsion between electrons. Once the wavefunction $\Psi$ is obtained by solving the Schrödinger equation, any experimental observable can be computed as the expectation value of appropriate operator, $\langle \Psi | O | \Psi \rangle$. In the case of total electronic energy, the operator is electronic Hamiltonian.

1.3.1 Hartree-Fock Theory:

The acceptable solutions of Eq (1.4) need to be necessarily well-behaved, i.e. wavefunction is finite, single valued, continuous, quadratically integrable and obeying the appropriate boundary conditions. Thus

$$\int \psi^*(r_1, r_2, ..., r_N)\psi(r_1, r_2, ..., r_N) d^3r_1 d^3r_2 ... d^3r_N = 1$$

(1.6)

Initial attempts by Hartree to devise such an approximate wavefunction of many-electron systems lead to the Hartree product (HP) function, which is a product of the one-electron functions and normally referred as orbitals. In this scheme, the spatial distribution of electrons has been defined in terms of spatial orbitals. These spatial orbitals are functions of the position vectors of electrons. To define an electron completely, in addition to the spatial coordinates the spin of electron is also required. Thus the notion of electronic spin is introduced in the one-electron function (orbital) by means of the spin functions $\alpha(o)$ and $\beta(o)$ that correspond to the up and down spin...
electrons, respectively. This leads to the spin orbitals, \( \{ \chi_i \} \) defined below.

\[
\chi_{3s}\,(x) = \psi_0^s(x)\alpha(\omega) \\
\chi_{3d}\,(x) = \psi_0^d(x)\beta(\omega)
\]  

(1.7)

where each electron is defined in terms of combined spatial and spin coordinates, \( x \).

Thus, the HP function can be written as

\[
\Psi^{1p}\,(x_1, x_2, ..., x_N) = \chi_{s}(x_1)\chi_{s}(x_2) .... \chi_{s}(x_N)
\]

(1.8)

The HP function is an independent-electron wavefunction and do not satisfy the antisymmetry principle. This requirement within the orbital picture is equivalent to the Pauli’s exclusion principle,\(^{20}\) which states that no two electrons of an atom shall have identical value of all the four quantum numbers \( n, l, m \) and \( s \).

Slater\(^{21}\) and Fock\(^{22}\) independently proposed that an antisymmetrized sum of all the permutations of HP functions would solve this problem for many-electron systems.

\[
\Psi(x_1, x_2, ..., x_N) = -\Psi(x_1, x_2, ..., x_N)
\]

(1.9)

This is achieved by using a determinantal form of function, later came to be known as the Slater determinant. Thus, an N-electron wavefunction within the HF formulation can be written as

\[
\Psi_{HF}\,(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}
\chi_{s}(x_1) & \chi_{s}(x_1) & ... & \chi_{s}(x_1) \\
\chi_{s}(x_2) & \chi_{s}(x_2) & ... & \chi_{s}(x_2) \\
... & ... & ... & ...
\end{vmatrix}
\]

(1.10)

The pre-factor \( 1/\sqrt{N!} \) ensures a normalized representation of the wavefunction. The spin orbitals are denoted as \( \chi \)'s, while \( x_1, x_2, ... \) etc. represent the combined spatial and spin coordinates of the respective electrons. The normalized Slater determinant can also be
represented in a shorter notation as
\[ \Psi(x_1, x_2, \ldots, x_N) = |\chi_1, \chi_2, \ldots, \chi_N \rangle \] (1.11)

In this notation (cf. Eq. 1.11), it is presumed that electrons 1, 2, etc. sequentially occupy the spin orbitals. The difficult task then lies in finding the appropriate set of spin orbitals, which is further complicated by introduction of the exchange-correlation term due to the determinantal form of wave function. The expectation value for the total electronic energy of a system, written in bra-ket notation is given by
\[ E_0 = \langle \Psi | H | \Psi \rangle = \sum_{a} \langle a|a \rangle + \sum_{a<b} \langle ab|ab \rangle \] (1.12)

In the above equation, the first term corresponds to one-electron integrals comprising of nuclear-electron attraction energy and kinetic energy of electrons. The second term is the electron-electron repulsion integral. The indices a and b refer to occupied spin molecular orbitals (MOs).

Using bra-ket notations introduced by Dirac the above one- and two-electron integrals can be expressed as
\[ \langle i|j \rangle = \int dx_1 \chi_1^*(x_1) \mathbf{h}_1(r_1) \chi_1(x_1) \] (1.13)
\[ \langle ij|kl \rangle = \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \mathbf{h}_1(r_1) \mathbf{h}_2(r_2) \chi_1(x_1) \chi_2(x_2) \] (1.14)
\[ \langle ij|kl \rangle = \langle ij|kl \rangle - \langle ij|k \rangle \] (1.15)

Eqs. (1.13) and (1.14) define the one- and two-electron integrals, while the LHS in Eq. (1.15) represents the combined Coulomb and exchange integrals. The essence of HF theory, in its simplest form, is in finding the best approximation to the GS of a many electron system, in the form of a Slater determinant, which minimizes energy of the system given in Eq. (1.12). The minimization is carried out within the framework of
variation principle: the expectation value of energy for a well-behaved trial function, obeying appropriate boundary conditions, is never lower than the corresponding energy obtained from an exact wavefunction.

\[
E = \frac{\langle \Psi_{\text{trial}} | H | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle} \geq E_0 = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \tag{1.16}
\]

Here, \(\Psi_{\text{trial}}\) and \(\Psi_0\) are the trial and exact wavefunctions respectively, of the system, while \(E\) is the expectation value for \(\Psi_{\text{trial}}\) and \(E_0\) the corresponding exact HF energy. Thus the best possible estimate for energy has been obtained by minimizing \(E\) with respect to the spin orbitals \(\{\chi_i\}\), with a constraint of orthonormality (cf. Eq. 1.17).

\[
\langle \chi_a | \chi_b \rangle = \delta_{ab} \tag{1.17}
\]

Such a minimization leads to the celebrated HF equations:

\[
f(i) \chi(x_i) = \epsilon \chi(x_i) \tag{1.18}
\]

where \(f(i)\) is the effective one-electron operator called the Fock operator and \(\epsilon\) is its eigenvalue (energies of spin orbitals). The success of HF method is in replacing the exact electron-electron interaction by an effective electron repulsion potential \(v^{\text{eff}}\), which is essentially a one-electron operator. The Fock operator is defined as

\[
f(i) = h(i) + v^{\text{eff}}(i) = h(i) + \sum_a \left[ J_a(i) - K_a(i) \right] \tag{1.19}
\]

The first term is the one-electron operator, called the core-Hamiltonian and is a sum of kinetic energy and nuclear-electron attraction energy operators, while \(J_a\) and \(K_a\) are the Coulomb and exchange operators, respectively. The Coulomb operator gives the electron-electron repulsion energy and the exchange operator provides lowering of energy due to correlation between electrons of same spin, an artifact of the determinantal
wavefunction. The operators $J$ and $K$ are defined by their operation on one-electron functions.

\[
J_s(l)\chi_s(l) = \left[\int dx_2 x_2 r_{12}^s \chi_s(2)\right] \chi_s(l) \\
K_s(l)\chi_s(l) = \left[\int dx_2 x_2 r_{12}^s \chi_s(2)\right]\chi_s(l)
\]

(1.20)  
(1.21)

It may be seen that the operators, $J$ and $K$, themselves are dependent on the eigenfunctions, the spin orbitals $\{\chi_s\}$. Hence, the HF equation is termed as pseudo-eigenvalue equation. In the matrix notation it is written as

\[
\begin{pmatrix}
\mathbf{f}^T \\
\end{pmatrix} = \mathbf{e}_s \begin{pmatrix}
\mathbf{\chi}_s \\
\end{pmatrix}
\]

Here, $\{e_s\}$ are the eigenvalues of Fock operator and denote the energies of spin molecular orbitals. Solving Eq. (1.22) results in a set of canonical spin orbitals that are delocalized and reflect the molecular symmetry.

### 1.3.1a Restricted Hartree-Fock (RHF) Theory:

For the closed-shell molecular systems where all the spatial orbitals are doubly occupied, RHF theory is used. The HF equations for this case are of the form

\[
f(r_i)\psi_i(r_i) = e_i \psi_i(r_i)
\]

(1.23)

Here, $\psi_i(r_i)$ is the spatial orbital where the spin functions are integrated out. The Fock operator within RHF framework is given by

\[
f(l) = h(l) + \sum_{s}^{N_s}[2J_s(l) - K_s(l)]
\]

(1.24)

The difference between Eqs. (1.24) and (1.19) is due to the vanishing of exchange integral when the electrons have opposite spin, which also accounts for one of the shortcomings in the HF theory.
Since the form of spin orbitals is not known, obtaining the solutions of integro-
differential for molecular systems is far from straightforward and such equations have to
be solved numerically. In 1951 Roothaan\textsuperscript{23} and Hall\textsuperscript{24} proposed a scheme to solve this
integro-differential equation. Thus these integro-differential equations can be transformed
into a set of algebraic equations by introducing known spatial basis functions \( \{ \phi_{\mu} \} \), which
are soluble using standard matrix techniques. The atomic orbitals (AOs) form the natural
choice of basis and hence the linear combination of atomic orbitals – molecular orbitals
(LCAO-MO) approximation is used in majority of the \textit{ab initio} calculations. Since the
exact form of AOs are not known for many electron systems, these are generally
represented in terms of Slater or Gaussian functions (see the subsection on Basis Sets for
further discussion on this). Thus, within LCAO-MO approximation the MO is given by

\[
\Psi_i = \sum_{\mu=1}^{k} C_{\mu} \phi_{\mu} 
\]  

(1.25)

where, \( C_{\mu} \)'s are the expansion coefficients and \( \{ \phi_{\mu} \} \) the Gaussian/Slater functions. The
total number of basis functions is specified as \( k \).

To arrive at the exact expansion one requires a set of infinite basis \( \{ \phi_{\mu} \} \).
However, for practical computational reasons, a finite set is always chosen. The
transformed HF equation is given by

\[
f(I) \sum_{\mu} C_{\mu} \phi_{\mu}(I) = e_i \sum_{\mu} C_{\mu} \phi_{\mu}(I) 
\]  

(1.26)

The basis sets, though can be chosen to be normalized, are not orthogonal, i.e.

\[
\int \phi_{\mu}^*(I) \phi_{\nu}(I) d^3 r_i \neq 0 \text{ unlike the case of MOs. This results in an additional term, the }
\text{overlap integral } S \text{ (between different functions of the basis) in the expression for expectation value of energy.}
\]
The new matrix-eigenvalue equation termed as Roothaan-Hall equations is used in most of the *ab initio* packages to implement HF calculations and has the form shown below

\[ FC = SC \varepsilon \]

(1.28)

where, \( F \) is the Fock matrix whose elements are computed as in Eq. (1.24), \( C \) the matrix of expansion coefficients and \( S \), the corresponding overlap matrix. The eigenvalue matrix \( \varepsilon \) is a diagonal matrix of orbital energies. The coefficient matrix has the form shown below.

\[
C = \begin{pmatrix}
C_{11} & C_{12} & \cdots & C_{1k} \\
C_{21} & C_{22} & \cdots & C_{2k} \\
\vdots & \vdots & \ddots & \vdots \\
C_{k1} & C_{k2} & \cdots & C_{kk}
\end{pmatrix}
\]

(1.29)

where \( k \) denotes the number of basis functions in the system. A solution to the HF equation involves solving the matrix eigenvalue equation (cf. Eq. 1.28) leading to the coefficient matrix, \( C \). Since the Roothaan-Hall equation is also a set of pseudo eigenvalue equations, it needs to be solved iteratively. An initial guess of spin orbitals provides an approximate effective one-electron potential, \( \psi_{\text{eff}} \). Solving the HF equation with the corresponding Fock matrix engenders a new set of spin orbitals, which in turn provides an improved \( \psi_{\text{eff}} \). The iterations are continued until the field due to \( \psi_{\text{eff}} \) and the electronic energies in two successive iterations do not vary above a predefined threshold, i.e. a self-consistency in the field is achieved and hence this process is termed self-consistent (SCF) procedure.
1.3.1b Unrestricted Hartree-Fock (UHF) Theory:

For open-shell systems, where the number of $\alpha$-spin electrons are different from that of $\beta$-spin electrons, it is essential to treat the $\alpha$- and $\beta$- spin orbitals separately. Such a treatment leads to two sets of eigenvalue equations:

\begin{align*}
\mathbf{f}^{\alpha}(1)\psi^{\alpha}(\mathbf{r}) & = \varepsilon\psi^{\alpha}(\mathbf{r}) & (1.30) \\
\mathbf{f}^{\beta}(1)\psi^{\beta}(\mathbf{r}) & = \varepsilon\psi^{\beta}(\mathbf{r}) & (1.31)
\end{align*}

where the Fock operators corresponding to $\alpha$ and $\beta$ spins are given by

\begin{align*}
\mathbf{f}^{\alpha}(1) & = \mathbf{h}(1) + \sum_{\alpha} \left[ \mathbf{J}^{\alpha}(1) - \mathbf{K}^{\alpha}(1) \right] + \sum_{\alpha} \mathbf{J}^{\alpha}(1) & (1.32) \\
\mathbf{f}^{\beta}(1) & = \mathbf{h}(1) + \sum_{\beta} \left[ \mathbf{J}^{\beta}(1) - \mathbf{K}^{\beta}(1) \right] + \sum_{\beta} \mathbf{J}^{\beta}(1) & (1.33)
\end{align*}

The summation limits $N_{\alpha}$ and $N_{\beta}$ are the number of electrons of $\alpha$ and $\beta$ spins respectively. The core Hamiltonian, $\mathbf{h}(1)$ is independent of the spin of electrons. However, since $\mathbf{f}^{\alpha}(1)$ has implicit dependence on $\chi^{\beta}$ and $\mathbf{f}^{\beta}(1)$ on $\chi^{\alpha}$, the equations (1.32) and (1.33) cannot be solved independently and a coupled iterative procedure is adopted. Expansion of the $\alpha$ and $\beta$ spin orbitals in terms of basis sets leads to the Pople-Nesbitt equations \(^{25}\) (cf. Eqs (1.34) and (1.35)), analogous to the Roothaan-Hall equations for RHF treatment.

\begin{align*}
\mathbf{F}^{\alpha}\mathbf{C}^{\alpha} & = \mathbf{S}^{\alpha}\mathbf{C}^{\alpha}\varepsilon & (1.34) \\
\mathbf{F}^{\beta}\mathbf{C}^{\beta} & = \mathbf{S}^{\beta}\mathbf{C}^{\beta}\varepsilon & (1.35)
\end{align*}

The total electronic energy for an unrestricted HF (UHF) calculation is computed as follows
Effecting an UHF calculation on a closed-shell system leads to solutions identical to that of RHF ones, unless other possibilities of lower energies exist. A solution to the Pople-Nesbet, however, an equation is computationally more intensive than the RHF counterpart.

1.3.1c Basis Sets:

Within the LCAO-MO approximation, MOs are expanded as linear combinations of AOs. However, since it is not possible to obtain the exact AOs for many-electron atoms, Slater type orbitals (STOs) were used to mimic AOs in the early days. Due to the difficulty in computing two- and other multi-center integrals using STOs, Boys suggested the use of standard Gaussian functions centered on atoms (GTO). A Cartesian Gaussian function used in electronic structure calculations has the form:

$$g(\alpha, l, m, n; x, y, z) = N_{l,m,n}(x-x_A)^{l}(y-y_A)^{m}(z-z_A)^{n}e^{-\alpha r_A^2}$$

(1.37)

where, $\alpha$ is the orbital exponent and $l, m, n$ are the powers of Cartesian components $x, y$ and $z$ respectively. The center of a Gaussian function is denoted by $r_A= (x_A, y_A, z_A)$. The computational advantage of GTOs over STOs is primarily due to the Gaussian product theorem, viz: the product of two GTOs is also a Gaussian function centered at the weighted midpoint of the two functions. In addition, the resulting integrals can be evaluated analytically. However, for the sake of computational convenience, it is a common practice to bunch together a set of GTOs with fixed coefficients, $d_i$ (cf. Eq. 1.38). Such a linear combination is termed the contracted GTO (CGTO).
The orbital exponents and contraction coefficients are determined from appropriate atomic
calculations. There are varieties of Gaussian basis sets available now, which have been
continuously improved over the years. The single-zeta Gaussian basis sets, also known,
as minimal basis set are the simplest GTOs. It consists of one CGTO per AO in shell and
provides a rather crude description of the electronic system. The STO-3G basis set, which
has been used extensively during the early days of molecular quantum mechanics,
is the most popular single-zeta basis set. For reliable qualitative results, however, it is
essential to use double-zeta basis functions that contain two CGTOs per AO in shell.
State-of-art calculations in recent years make use of triple-zeta basis functions. In
addition, the extended basis sets include basis function of higher angular momentum
than those present in the basis. This ensures adequate representation of polarization of
the electronic charge density. Similarly, it is essential to add the diffuse functions to the
basis set when the regions of low ED in the system are of great interest. There is also a
wide range of customized basis sets. The most frequently used being the Pople’s split
valence basis set (multiple CGTOs for valence shells only) with a varying number of
polarization functions such as 6-31G(d,p), 6-311++G(2d,2p) etc., Dunning basis set
and the correlation consistent valence double and triple zeta basis functions (cc-pvdz,
cc-pvtz).

1.3.2 Semi-empirical Methods:

The demand for theoretical methods that can tackle large molecules is ever
increasing. Although the pure ab-initio quantum chemical programs incorporates the HF-
SCF and further, correlated procedures give quantitative predictions, such methods are
almost impossibly to apply on chemical problem that involve the simultaneous treatment of a large number of atoms such as large cluster of atoms, solvating processes, polymer reactions, folding of proteins etc. Semi-empirical quantum chemical methods are in general, designed for such purposes. They combined fundamental theoretical treatment of electronic behavior with parameters obtained from experiments to obtain approximate wavefunctions for large molecules. Many semi-empirical methods work within the framework of HF theory in the HF method, Roothaan equations is most difficult task which scales as N^4, where N is the number of basis functions used to obtained Mos. The bottleneck problem is the computation of two electron integrals, which even for a small molecule can go up to several millions! In semi-empirical methods the two electron integrals are obtained in terms of atomic parameters generated through fitting the results with experimental data such as heats of formation, atomization energies etc. This keeps semi-empirical algorithms for obtaining many-electron wavefunctions to N^3 or N^2 scale, allowing larger systems to be treated by these methods relative to ab-inito methods. The Hückel theory formulated as early as 1931 falls into the second type. It treats only the π-electrons and is applicable to planar π-systems. The atomic parameters α and bond parameters β completely replace the electron repulsion integrals (ERIs) and hence the SCF procedure is not required. Solving the resulting secular determinant is relatively simple and the Hückel method is often referred to as a back-of-envelope method. This simple model could successfully predict resonance energies and orbital symmetries. An extension of this model, the extended Hückel theory (EHT), which includes valence σ-electrons in the treatment and can handle hetero atomics, is still being used. The seminal work by Woodward and Hoffmann that lead to the famous Woodward-Hoffmann rules
for pericyclic reactions used energies and orbitals from EHT calculations. Another π-electron model worth mentioning is the Pariser-Parr-Pople\textsuperscript{42-43} (PPP) method, which allows better treatment of aromatic systems. The two-electron MO methods generally employ the neglect of differential overlap (NDO) approximation using different conditions to ignore orbital overlaps. The overlap (Eq. 1.39) and two electron (Eq. 1.40) integrals within Zero Differential Overlap (ZDO) are given as

\[
\phi_\sigma^\ast (\mathbf{r}) \phi_\sigma (\mathbf{r}) = \delta_\nu \nu
\]

(1.39)

\[
\langle \mu \nu | \lambda \sigma \rangle = \delta_\mu \lambda \delta_\nu \nu \langle \mu \nu | \mu \nu \rangle
\]

(1.40)

The NDO methods use extensive parametrization. The core electrons are not treated explicitly; instead a core-core repulsion function is used to represent them. The complete and intermediate (CNDO\textsuperscript{14} and INDO\textsuperscript{45}) NDO methods and their variations were able to produce accurate orbitals and properties like charge densities and dipole moments. The currently popular semi-empirical methods such as MNDO\textsuperscript{46}, AM1\textsuperscript{17} and PM3\textsuperscript{48} have minimal neglect of differential overlap and differ primarily in the parameters used i.e. on the set of compounds used for fitting the parameters. In these models, the differential overlap is ignored only if the orbitals are on neighboring atoms. They are very efficient and the molecular geometries and properties produced by them are comparable with low level \textit{ab initio} calculations. Many of the popular \textit{ab initio} packages provide semi-empirical calculations. The package MOPAC\textsuperscript{49} implements most of these methods and is widely used for semi-empirical calculations. The recent release of this program, MOPAC-2000\textsuperscript{50} includes the module MOZYME that promises feasibility of computations on enzymes and other biomolecules containing several thousands of atoms.
1.3.3 Post-HF Methods:

The electron in a molecule exhibits a correlated motion, i.e., each electron moves in a way that avoids the instantaneous positions of the other electrons. This is called the coulomb correlation. In the HF method the motion of electrons with opposite spins are not correlated i.e. the instantaneous probability of finding two electrons having opposite spins and occupying the same space is non-zero. This results in a higher total energy at the HF level. In addition, the quantities computed from HF calculations are known to have errors to various degrees. For example with the HF theory, the bond lengths of organic compounds are too small, the orbital ordering of N\textsubscript{2} is wrong, it predicts longer metal-\pi bonds and high heats of formation to name a few. The H\textsubscript{2} homolytic cleavage is a well-known case for the failure of the HF theory. Though UHF calculations explain such a homolytic cleavage, the potential energy surfaces constructed using UHF are unrealistic. Such factors focus the need for further accurate methods that would produce results in coherence with the experimental counterparts. The post-HF methods try to obtain the correlation energy \( E_{\text{corr}} \), defined\textsuperscript{51} as the difference between the exact \textit{ab initio} energy and exact (complete basis) HF energy, \textit{viz.}

\[
E_{\text{corr}} = E_y - E_0
\]  

(1.41)

where, \( e_y \) is the exact eigenvalue of \( H_{\text{elec}} \) and \( E_0 \) the “best” HF energy with the basis set extrapolated to completeness. The two popular approaches that try to compute \( E_{\text{corr}} \) are the configuration interaction\textsuperscript{52,53} (CI) and many body perturbation theory\textsuperscript{54-55} (MBPT) methods. The next two Sections provide a summary of these methods.
1.3.4 Configuration Interaction:

The CI is conceptually one of the simplest methods to estimate E\textsubscript{corr}. (See ref. 32 for a comprehensive review on CI methods). It is a variational method, wherein the Hamiltonian is constructed in a basis of Slater determinants. The complete CI wavefunction is a linear combination of Slater determinants with all the permutations of electron occupancies expanded as shown below.

\[ |\Phi_0\rangle = c_a |\Psi_0\rangle + \sum_{a>b} c^{ab}_{\text{ab}} |\Psi_{\text{ab}}^{(1)}\rangle + \sum_{a>b>c} c^{abc}_{\text{abc}} |\Psi_{\text{abc}}^{(1)}\rangle + \ldots \]  \hspace{1cm} (1.42)

The first term in Eq. (1.48) represents the Slater determinant corresponding to the HF wavefunction and rest of the terms constitute singly, doubly, triply... n-tuply excited determinants with appropriate expansion coefficients. The indices a,b,r,s, etc. signify the occupied and virtual orbitals involved in the electron excitations. It is a convention to use the indices a, b, c... for occupied orbitals and r, s, t... for the virtual ones.

In the single-reference CI, the HF wavefunction is used as the reference determinant and the energy is minimized variationally with respect to the determinant expansion coefficients. However, as the number of electrons in the system increases, there is an explosive growth in the number of configurations (determinants) and it is nearly impossible to treat the complete configurational space even with the present day supercomputers. The number of n-tuply excited determinants for a system of N electrons is given by the product of combinations, \(^NC_n \cdot (2k-n)C_n\) where 2k is the number of spin orbitals in the system. Hence for practical reasons, the wavefunction expansion is truncated up to a certain excitation level. The simplest CI method includes only the doubly excited determinants (DCI). Brillouin\textsuperscript{55} proved that the singles (here and
elsewhere in the thesis singles, doubles, etc. mean singly, doubly etc. excited determinants, respectively) do not mix directly with the HF wavefunction. Hence the energy does not improve significantly by including only the singles in the CI wavefunction expansion (CIS). Nonetheless, the CIS calculations have been found extremely useful in predicting the excited state geometries, energies and electronic spectra of molecules. In addition, the singles contribute indirectly to the correlation energy of GS by interacting with doubles and hence the most commonly used CI approach is the CISD method.

Calculations using the wavefunctions, which include higher order excited determinants such as QCISD, are prevalent (for small molecules) in the literature. For further accurate results, one can perform multi-reference CI calculations, wherein the Slater determinants in each configuration are also allowed to vary. Though the truncated-Cl calculations produce reasonable estimates of correlation energy, the results are not size-consistent (energy of a system of non-interacting constituents equals sum of the energies of individual constituents) and size-extensive (energy being proportional to the number of particles in the system).

1.3.5 Perturbation Theory:

The basis of perturbation theory (PT) lies in partitioning an insoluble problem into a soluble part and an insoluble fraction. The exact solution to the first part is then perturbed successively to evolve a solution to the total system. Since the complete mathematical foundations of PT were laid much before the birth of QM, immediately after the formulation of Schrödinger equation, it was subject to perturbative treatment. The Rayleigh-Schrödinger Perturbation Theory (RSPT) is the most widely accepted
method in use. If $H^{(0)}$ be a part of the complete QM Hamiltonian and its exact
eigenfunctions $|\Psi_i^{(0)}\rangle$ are known, then the total Hamiltonian of the system is written as

$$H = H^{(0)} + \lambda H'$$

(1.43)

where, $H'$ is the perturbation applied to the soluble Hamiltonian $H^{(0)}$ and $\lambda$ is the
perturbation parameter ($0 \leq \lambda \leq 1$). Eigenfunctions of the total Hamiltonian are expanded
as a Taylor series in $\lambda$ as

$$|\Phi_i\rangle = |\Psi_i^{(0)}\rangle + \lambda |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \ldots.$$

(1.44)

The exact eigenvalue then takes the form

$$\varepsilon = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots.$$

(1.45)

In Eq. (1.45), the expansion coefficients sequentially constitute the zeroth, first, second,
etc., up to $n$th order energies, respectively.

Substituting Eqs. (1.42–1.44) into the Schrödinger equation results in terms with various
powers of $\lambda$ on both the LHS and RHS of equation. Equating terms that have same
powers in $\lambda$ leads to a set of relations referred to as zeroth (cf. Eq. 1.46), first (cf. Eq.
1.47), second (cf. Eq. 1.54) and successive order perturbation equations.

$$H^{(0)}|\Psi_i^{(0)}\rangle = E_i^{(0)}|\Psi_i^{(0)}\rangle$$

(1.46)

$$H^{(0)}|\Psi_i^{(1)}\rangle + H'|\Psi_i^{(0)}\rangle = E_i^{(0)}|\Psi_i^{(1)}\rangle + E_i^{(1)}|\Psi_i^{(0)}\rangle$$

(1.47)

$$H^{(0)}|\Psi_i^{(2)}\rangle + H'|\Psi_i^{(1)}\rangle = E_i^{(0)}|\Psi_i^{(2)}\rangle + E_i^{(1)}|\Psi_i^{(1)}\rangle + E_i^{(2)}|\Psi_i^{(0)}\rangle$$

(1.48)

Solving these equations individually, furnish energy correction terms of appropriate order
as defined below.

$$E_i^{(n)} = \langle \Psi_i^{(0)} | H^{(0)} | \Psi_i^{(0)} \rangle$$
Møller and Plesset were the first to employ RSPT to N-electron systems using the HF Hamiltonian as $H^{(0)}$, a good starting point since in this case, $H^{(0)}$ is the Fock operator and it is possible to obtain its exact solutions. In this approach, the $H - H^{(0)}$ is given by the difference between the sum over exact electronic potential, $r_{ij}^{-1}$ and the effective one-electron potential, $u^{HF}$ used in the HF theory, i.e.

$$H' = \sum_{i<j} r_{ij}^{-1} - \sum_i u^{HF}(i)$$

$$= \sum_{i<j} r_{ij}^{-1} - \sum_i \sum_x [J_x(i) - K_x(i)]$$

(1.50)

The perturbed wavefunctions of various orders are expanded in a basis of the HF and excited state determinants (cf. Eq. 1.51).

$$|\Psi_i^{(k)}\rangle = \sum_{\mu=0}^{k} C_{\mu}^{k} |\Psi_i^{(k)}\rangle$$

(1.51)

where, $k$ represents the order of the function and $\mu$, the order of excitation. The energy correction terms in Møller-Plesset perturbation theory (MPPT) can be obtained by appropriate substitutions in Eq. (1.48) The above terms turn out to be

$$E_0^{(0)} = \sum_a \alpha_a$$

(1.52)

$$E_0^{(1)} = -\frac{1}{2} \sum_{a,b} \langle ab \parallel ab \rangle$$

(1.53)

$$E_0^{(2)} = 2 \sum_{ab,rs} \frac{\langle ab \parallel rs \parallel ab \rangle - \sum_{x} \langle ab \parallel rs \parallel ba \rangle}{E_a + E_b - E_x - E_y}$$

(1.54)

Hence the total energy, correct up to second order, is
since the first two terms summed together gives the HF energy. Thus, the leading correction term in the MPPT is $E_0^{(2)}$. Brueckner\textsuperscript{63} and later, Goldstone\textsuperscript{53-54} through diagrammatic technique,\textsuperscript{64} have shown that all the energy correction terms are size-consistent. MBPT results are also size-extensive, unlike the truncated-CI methods. The equilibrium geometries, dissociation energies and energy difference between various electronic states from MBPT are more accurate than the HF counterparts.\textsuperscript{52} The energies from MBPT, however, are non-variational and in other words do not provide an upper bound to the exact energy. For extended systems, which warrant size-extensive methods and studies involving weak complexes that require size-consistent methods, MBPT is the preferred approach over the variational post-HF methods. On the other hand, chemical reactions involving bond breaking and bond formation require the use of multi-configuration wavefunction methods rather than PT-based approaches.

Other high level correlated methods that yield accurate correlation energies are the coupled cluster\textsuperscript{55-60} (CC) and multi-configuration SCF\textsuperscript{67-68} (MCSCF) methods. Though the CC approach was developed in the late 1960’s, it was the re-derivation of CC equations by Čiček and Paldus\textsuperscript{69-70} that made it popular among quantum chemists. The pioneering work by Bartlett and coworkers\textsuperscript{71} and the developments that followed have made CC the most accurate and computationally affordable method for small molecules. The CCSD (CC with single and double excitations) provides about 95 percent of the correlation energy. The state-of-art correlation calculations widely reported in the literature involve CCSD(T) \textit{i.e.} CC with singles and doubles with a perturbative
treatment to add triples, which yields energies that are closest to its experimental counterparts. This method, however, scales as (non-iterative) $O(N^7)$ and cannot be employed to systems with more than ~10 atoms. Similarly, the CASSCF (complete active space SCF) a variant of MCSCF, has found practical utility only for small molecules. Unlike these rigorous \textit{ab initio} methods, the DFT offers a substantial improvement over HF energy without consuming much additional computation time.

\subsection{1.3.6 Density Functional Theory:}

Density functional study endows the single particle density $\rho(r)$, the status of a basic entity and justifies its usage as a fundamental quantity on a rigorous, general rational footing that has stimulated a widespread interest in recent years. There are several advantages over the conventional wavefunction approach to quantum mechanics. First, the wavefunction for an $N$-electron system is a function of $3N$ spatial co-ordinates whereas the density $\rho(r)$ is dependent only on three independent spatial co-ordinates (or four, if the spin is included). Second, the density $\rho(r)$ is an observable, subject to a measurement experimentally while the many-particle wavefunction is an intangible entity. Third, the density is a very conventional parameter for a collective description of many-electron system wherein single particle co-ordinates lose their indentity.

Thomas\textsuperscript{72} and Fermi\textsuperscript{73-74} (TF) developed a statistical model, wherein the total electronic energy of a system was expressed as a functional of the charge density distribution, $\rho(r)$. The kinetic energy functional, $T_{\text{TF}}[\rho]$ derived by them is

$$T_{\text{TF}}[\rho] = \frac{3}{10} (3\pi^2)^3 \int d^3 r \rho^\frac{5}{3}(r) \quad (1.56)$$

The total TF energy is obtained by adding the contributions due to Hartree (Coulomb)
potential to Eq.(1.56) They assumed the local homogeneity of the inhomogeneous density distribution. Though the TF model has been augmented with corrections in the later years,\textsuperscript{9,75} it remained as a simple qualitative model until the formulation of coveted Hohenberg-Kohn (HK) theorems.\textsuperscript{8} The HK theorem finally laid the foundation of the DFT. In this theory, the electron density plays the role of basic variable. The HK theorems may be stated as:

\begin{itemize}
  \item[i)] \textit{The external potential is determined, within an additive constant, by the ground state ED.}
  \item[ii)] \textit{The energy due to any normalized, non-negative trial density that satisfies certain conditions is variational.}
\end{itemize}

These theorems laid foundation to the modern DFT. Eq. (1.57) represents the second theorem

\[ E^0 \leq E[\rho(r)] \]  

(1.57)

where, $E^0$ is the exact energy. In DFT, the electronic energy functional is expressed in terms of the (cf Eq. 1.58) contributions due to kinetic energy $T$, external potential $V$ and the electron-electron interaction energy $U$.

\[ E[\rho] = T[\rho] + V[\rho] + U[\rho] \]  

(1.58)

However, Eq. (1.64) has relevance only if there exists an external potential, $V$ for a given trial $\rho(r)$. Levy\textsuperscript{76-78} overcame this problem of $V$-representability noticed by Larsson\textsuperscript{79} through a constrained-search approach.

Despite these developments, a practical solution was elusive since the exact form of functionals $T$ and $U$ were not known. Kohn and Sham\textsuperscript{9} (KS) introduced the concept of orbitals into DFT in 1965. Since the GS density of non-interacting system may be treated
as the GS density of completely interacting system, the KS formalism gives unique set of orbitals for a given density. Applying the HK variational principle with respect to the KS orbitals yields the following canonical KS orbital equations, analogous to the HF equations:

\[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})\]  \hspace{1cm} (1.59)

It should be noted here that the effective potential operator $V_{\text{eff}}$ is independent of the index of electron and is much simpler than the effective one-electron potential in the Fock operator. The effective potential (cf. Eq. 1.59) is a sum of external potential $V_{\text{ext}}$, the electron-electron Coulomb potential and the exchange-correlation potential $V_{xc}$ as given below.

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d^3 r' \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r})$$  \hspace{1cm} (1.60)

The exchange correlation potential, $V_{xc}$ is a functional derivative of the form

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$$  \hspace{1cm} (1.61)

Eq. (1.59) is a set of nonlinear equations much like the Roothaan-Hall equations and is to be solved iteratively by SCF procedure. Within KS formalism, the total electronic energy of the system is computed as

$$E_{se}[\rho] = \sum_i \varepsilon_i - \frac{1}{2} \int d^3 r d^3 r' \frac{\rho(r) \rho(r')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] - \int d^3 r V_{xc} \rho(\mathbf{r})$$  \hspace{1cm} (1.62)

where the first term is the sum of orbital energies and the last term is due to derivative of the KS exchange correlation functional.

Even the HK and KS formalisms do not lead to the exact form of exchange-
correlation functional \( E_{XC}[^{\rho}] \), much of it is left to a systematic search and guesswork. Thus a variety of exchange-correlation functionals exist in literature,\(^8\)\(^9\) which are generally integrals of some function of ED. The Slater’s \( X_\alpha \) method\(^8\)\(^2\)\(^,\)\(^3\) is considered the predecessor of modern DFT methods. Slater replaced the exact exchange potential term in HF equation by a statistical one given by

\[
V_{X_\alpha}(r) = -6\alpha \left[ \frac{3}{4\pi} \rho(r) \right]^{1/3}
\]

The value of \( \alpha = 1 \) is prescribed in the original formulation by Slater. The local density approximation (LDA) has been made in deriving Eq. (1.63) Gáspár\(^4\)^ and later, Kohn and Sham\(^9\)^ suggested that \( \alpha \) in the coefficient should hold a value of 2/3 instead of 1, i.e. \( \alpha \) times Slater’s potential and hence the method gained a generic name, \( X_\alpha \). This had been the most successful method for decades until newer functionals within KS formalism were introduced. A notable difference came with the generalized gradient approximation\(^5\)(GGA) where, in addition to the density values, the functionals are dependent on the gradient of densities. The GGA functionals have the general form

\[
E_{\omega} = \int \left( \rho_{\omega}, \rho_{\beta}, \nabla \rho_{\omega}, \nabla \rho_{\beta}, \nabla \rho_{\omega}, \nabla \rho_{\beta}, \nabla \rho_{\omega}, \nabla \rho_{\beta} \right) d^3r
\]

The most widely used exchange functionals are Slater’s \( X_\alpha \)\(^8\)\(^2\), \( B88 \) (Becke’s 1988 functional that includes Slater’s exchange with gradient corrections), having the form as

\[
E_{X_{\alpha}} = E_{\text{LDA}}^{XC} - \gamma \int \frac{\rho^{4/3} x^2}{(1 + 6 \gamma \sin^{-1} x)} d^3r
\]

where \( x = \rho^{-1/3} \nu \rho \) and \( \gamma \) is a parameter chosen to fit the exchange energy of inert gas atoms (0.0042 a.u. as defined by Becke). Similarly, there exit local and gradient-corrected correlation functionals. Amongst the other functionals, available are VWN and
VWN5 by Vosko, Wilk and Nusair (1980), P86 and PW91 by Perdew and Wang (1992) etc. their details may be found elsewhere.

There also exits another type of functional, which offers some improvement over the corresponding pure DFT functional. This includes a mixture of HF and DFT exchange along with DFT correlation.

In above expression c’s are appropriate constant. The popular functional BLYP is obtained by coupling of Becke’s generalized gradient corrected exchange functional with the gradient corrected correlation functional of Lee, Yang and Parr. Becke was the first do use this methodology (1993) and he proposed B3PW91 functional, bearing the following form.

\[
E_{xc}^{\text{B3PW91}} = E(1-a)E_x^{\text{LSDA}} + aE_x^{\text{HF}} + b\Delta_x^{\text{B88}} + E_c^{\text{LSDA}} + cE_c^{\text{PW91}}
\]

Where a, b, c have optimized values of 0.20, 0.72 and 0.1 a.u. respectively. the name indicated the implementation of three-parameters scheme as well as use of Becke and PW91 functional.

Yet another popular hybrid functional is B3LYP. Becke-3 parameters non-local exchange functional, with the non-local correlation functional of Lee et al., functional having the form:

\[
E_{xc}^{\text{B3LYP}} = E(1-a)E_x^{\text{LSDA}} + aE_x^{\text{HF}} + b\Delta_x^{\text{B88}} + E_x^{\text{VWN3}} + (1-c)E_c^{\text{LSDA}} + cE_c^{\text{LYP}}
\]

Since the KS-scheme involves a variational procedure to arrive at the KS orbitals, it is expected that the energies from this formalism would be variationally bound. However, the exchange-correlation functionals have a strong parametric dependence and hence practically the energies obtained from KS-based methods are not variational. Recently, Becke has benchmarked his exchange-correlation functionals against the G1 (The
Gaussian-1 theory is an elaborate procedure for obtaining highly accurate energies through a series of calculations at predefined levels and basis sets) database generated by Pople and coworkers. A mean absolute error in the heats of atomization of 55 test molecules turns out to be 2.4 kcal mol$^{-1}$. Apart from the total electronic energy, there are certain other molecular properties rigorously defined within the DFT. Parr defined the electronic chemical potential of a system as the first derivative of energy (cf. Eq. 1.68) with respect to the number of electrons N and identified it with the negative of its electronegativity.

$$\mu = \left( \frac{\partial E}{\partial N} \right)$$  \hspace{1cm} (1.68)

The curvature of energy with respect to the number of electrons is also related rigorously in the hard-soft acid-base (HSAB) principle and the hardness is given by

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)$$  \hspace{1cm} (1.69)

These two quantities are being extensively used in the recent years.

In summary, DFT provides an economical alternative for treating molecules at correlated level of theory. However, disadvantage of DFT is the exchange-correlation functional, which cannot be derived rigorously from first principles. As of today, DFT remains an attractive alternative to more rigorous methods, such as CI.

1.4 Molecular Properties:

Atoms and molecules exhibit three types of properties. i) those displayed by the charge density distribution of electrons, by virtue of their interaction with other electrons and nuclei, and its functional derivatives. ii) those evidenced as a response to the
internal/external electric and magnetic fields and iii) those arising out of transitions in electronic, vibrational and rotational states by an interaction with electromagnetic radiation. The last two categories are not within the scope of the present work and hence no reference is made to them. The density-based properties can be further classified as point-dependent and point-independent properties. The point-dependent properties include scalar fields such as ED, electrostatic potential (ESP) \( V(\mathbf{r}) \), Laplacian of density \( \nabla^2 \rho \), density in momentum space and vectors fields such as the gradients of ED \( \nabla \rho \) and ESP \( -\nabla V \), electric field. The point-independent (overall) properties are dipole moment \( \mu \) and electronic energy \( E \). Among the above-mentioned properties, ED and ESP have found widespread applications in chemistry and biology. The following sections provide a detailed description of ED and ESP with a short note on the Laplacian of density and dipole moment.

1.4.1 Molecular Electron Density and Topography:

The distribution of an electron in the field due to other electrons and the collection of nuclei form the electronic property of foremost interest to chemists. It holds the key to understanding the chemical behavior of a collection of atoms, bonded or otherwise. In QM, ED is postulated for a one-electron function \( \Psi_\sigma(\mathbf{r}) \) as the probability distribution function \( |\Psi_\sigma(\mathbf{r})|^2 \). In general, for an N electron system ED is defined as

\[
\rho(\mathbf{r}) = N \sum_\sigma |\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 d^1 r_1 d^1 r_2 ... d^1 r_N
\]  

(1.70)

The summation in Eq. (1.70) is over \( \sigma \), the spin function of electrons. For methods that use single determinantal form of wave function such as HF/DFT which work in terms of orbitals, MED can be computed in terms of the density matrix (DM) as follows
where, $\phi_\mu$ and $\phi_\nu$ are the basis functions, resulting from LCAO-MO approximation.

Much of the chemical meaning derived from the analysis of MED is due to the pioneering work by Bader and coworkers. Since MED is a scalar field, to analyze and understand its properties, it is useful to have the aid of 3D-graphics visualization tools. In general, MED is evaluated over a 3D-grid encompassing the molecule and the analyses are carried out in terms of iso-valued contour and surface plots or textured planes. Alternatively, one can locate the topography (Greek: mapping of a place) of MED to analyze its silent features. Bader pioneered the topological concepts to study ED and its Laplacian.

Consider a 3D-scalar field $f$. In each direction, $f$ can be a local maximum or minimum. Thus, it engenders four types of topological features: maxima, minima and two types of saddle points. Any point in space where all the first-order partial derivatives of a function vanish ($\partial^2 f / \partial x_i = 0$ for $i=1,3$) is termed as a critical point (CP) of $f$. The topological feature of such a point, $P$ is characterized in terms of the rank and signature of its Hessian matrix, which is defined as

$$H_p = \frac{\partial^2 f}{\partial x_i \partial x_j}$$

The rank is defined as the number of non-zero eigenvalues of the Hessian matrix and signature, as algebraic sum of the signs of non-zero eigenvalues. Thus a CP is characterized as $(R, \sigma)$ where, $R$ is the rank and $\sigma$ the signature of CP of $f$. Hence, any 3D scalar function can have four types of non-degenerate CPs viz., $(3, +3)$ corresponding to a local minimum, $(3, +1)$ and $(3, -1)$ that represent saddle points on the surface and
finally, a (3, -3) that represents local maximum. However, not all these features are necessarily exhibited by the density of every molecule.\textsuperscript{92}

A pseudo maximum, which obeys Kato’s cusp condition\textsuperscript{93} \( \left[ \frac{\partial^2 \rho(r)}{\partial r^2} \right]_{r=0} = -2Z\rho(0) \) is observed at every nuclear position in atomic and molecular ED’s. Any two atoms that fall within a moderate distance, indicating a strong or weak bonding interaction between them, exhibit a (3, -1) saddle point. A set of bonded (strong or weak) atoms forming a ring possess a (3, +1) CP at the center of the ring, while a closed cage formed by bonded atoms has a minimum (3, +3) at its center. However, chemists are generally interested in the bond critical point (BCP) characterized as (3, -1). A relation between bond length and the bond order had earlier been established by Coulson.\textsuperscript{93} Bader\textsuperscript{94,95} and coworkers proposed an exponential relation between the density at the BCP, \( \rho_b \) and the bond order for a series of hydrocarbons. A similar analysis was later carried out by Boyd \textit{et al.}\textsuperscript{96} for a wide range of bond types. Further, the curvature at \( \rho_b \) gives insight into the nature of bond and explains features of \( \pi \)-bond, bent bond, etc. The bonds can also be characterized in terms of the ellipticity\textsuperscript{97} \( \varepsilon \) given by

\[
\varepsilon = \left[ \frac{\lambda_1}{\lambda_2} - 1 \right]
\]

where, \( \lambda_1 \) and \( \lambda_2 \) are the principal eigenvalues of the Hessian of ED at BCP, the former being higher in magnitude than the latter. Bader and co-workers\textsuperscript{92} employed ED to build a rigorous QM basis for the definition of an atom in a molecule (AIM). The AIM approach has hence been widely employed to partition MED and other derived properties into atomic components.
1.4.2 Molecular Electrostatic Potential:

The classical Coulombic electrostatic potential, $V(r)$ at the point $r$ due to a discrete point charge $q$, placed at $r_j$ is given by

$$V(r) = \frac{q_j}{|r - r_j|} \quad (1.74)$$

Since electrostatic potential (ESP) obeys the principle of superposition, the ESP at a point $r$ due to a collection of discrete charges $\{q_i\}$ located at $\{r_i\}$ can be written as

$$V(r) = \sum_i \frac{q_i}{|r - r_i|} \quad (1.75)$$

If instead of discrete charges, we have a continuous distribution of charge over space, the summation is replaced by integration over the entire space, i.e.

$$V(r) = \int \frac{\rho(r')dV'}{|r - r'|} \quad (1.76)$$

In Eq. (1.76) $\rho(r')$ is the continuous charge distribution.

Unlike other properties and observables, the ESP does not have a simple QM operator and its QM description is given by:

$$V(r) = \sum_{\alpha} \frac{Z_{\alpha}}{|r - R_{\alpha}|} - \int \frac{\rho(r')dV'}{|r - r'|} \quad (1.77)$$

Here, $\{Z_{\alpha}\}$ are the nuclear charges, while $r$ and $\{R_{\alpha}\}$ denote the position vectors of electrons and nuclei, respectively. Thus the ESP of atoms and molecules is comprised of two terms. One positive term due to the discrete nuclear charges, $Z_A$ and a negative term due to continuous distribution of electrons obtained from the atomic/molecular wavefunction. The opposing contributions from the two terms endow MESP with rich topological features. The atomic ED tends to zero at $r=\infty$ and positive at all other...
regions. On the contrary, MESP can have negative values and this necessitates additional caution in topological analysis of its scalar field. Atomic ESPs, however, do not possess negative values away from the atom center. In addition, atomic ESP is a monotonic decreasing function much similar to the atomic densities, but unlike atomic EDs, potential of atoms do not exhibit finite-valued nuclear maxima. The ESP at nuclear sites shows a discontinuity and negative value since the nuclear contribution from the corresponding atom is dropped out. Nevertheless, every atom is considered to possess a MESP maximum at its center. The monotonic decreasing atomic ESP is expected to achieve zero at infinite distance from the atom center and this feature is referred to as an asymptotic CP (minimum), which has greater significance in the case of molecules. Gadre et al.\cite{100-101} have proven the absence of non-nuclear maxima in ESP of molecules. Further work carried out by Gadre et al.\cite{102,103} has resulted in elaborate topographical analysis of MESP similar to that discussed for MED.

MESP brings out electron rich regions in the form of (3, +3) minima *vis-a-vis* lone-pairs of electrons and π-bonded electron pairs are exhibited as minima at the corresponding position near the van der Waals surface. Any bonding (covalent/weak) interaction between atoms is featured by the presence of a bond saddle (3, -1). Similar to the MED topography, these BCPs bring out the strain in bonds by deviating from the line joining the corresponding atoms. However, unlike the BCPs of MED, the MESP bond critical points of strained rings and cages lie within the ring/cage. This feature is in fact more prominent for MESP than the MED counterpart. A (3, +1) saddle generally connects two MESP minima. Unlike in the case of MED, the (3, -1) CP for MESP may also lie at the external molecular region such as in the case of benzene. For example, in
the case of water molecule two (3, +3) minima occur at tetrahedral sites with reference to the O–H bonds signifying the lone pairs of electrons. These two CPs are connected through a (3, +1) saddle lying along the C$_{2v}$ symmetry axis. There is one bond CP for each O–H bond. The region above oxygen atom (assuming the molecule is oriented with both the hydrogen atoms pointing down) is negative throughout and decays as $-q/r$, while the region below the hydrogen atoms is positive throughout and decays as $q/r$, leading to an asymptotic maximum and asymptotic minimum respectively. Similarly, the MESP of benzene molecule possess distinct features. Since benzene is a completely conjugated system, every C–C bond has equal $\pi$-character and each of them exhibit two (3, +3) minima one each on either side of the ring plane. These minima are linked to their neighbors through six (3, +1) saddles lying on either side of the ring. All these features together depict a crown like shape on both the sides of ring plane centered by (3, -1) - saddles. There is also a (3, +1) CP (ring) at the center of the ring plane.

The significance of the negative-valued MESP and their critical points in molecules and their anionic species have been widely dealt in the literature.$^{104}$-$^{108}$

1.4.3 Natural bond orbital analysis:

A localization algorithm that hews particularly closely to intuitive chemical concepts in the natural bond orbital (NBO) method of Weinhold and coworkers.$^{109}$ Orbitals that are associated almost entirely with a single atom (core orbitals and lone pairs) are localized as so called natural atomic orbital (NAOs). Next orbitals involving bonding between pair of atoms are localized by using the basis set AOs of those atoms. Finally the remaining Rydberg-like orbitals are identified and all orbitals made orthogonal to one another. The result is that all AOs of a single atom and all NBOs are
described using 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 to each atom’s contributions to its bond orbital. With the NBO analysis, the percent s and p character is immediately evident from the coefficients of the AOs basis functions from which the NAO or NBO is formed. In addition, a population analysis can be carried out using the NBO derived partial atomic charges. NBO analysis can be used to quantify the useful chemical concept hyperconjugation, which rationalizes certain chemical phenomenon in terms of filled orbital – empty orbital interactions. It must be stressed that the NBO procedure is only a conceptual model, since it is based on orbitals, and limitations in its utility may be expected in case where chemical species are poorly represented as Lewis structures.

1.4.4 Molecular Vibrations: 110

The vibrational frequencies are of great interest from the theoretical and experimental point of view. The vibrational frequency provides a way to characterize the molecular interactions present in the complex. Further, the derived vibrational frequencies predicts the nature of the minima or saddle on the potential energy surface. Following discussion pertains the calculations of vibrational frequency within theoretical framework and related concepts.

Within the framework of Born-oppenheimer approximation one calculates the total electronic energy $E_e$ for fixed nuclear coordinates (nuclear spins are ignored) can be (approximately) written as:

$$\vec{X} = (\vec{R}_1, \vec{R}_2, ..., \vec{R}_M) = (R_{1,x}, R_{1,y}, R_{1,z}, R_{2,x}, R_{2,y}, R_{2,z}, ..., R_{M,x}, R_{M,y}, R_{M,z})$$

(1.78)
The total energy

\[ E = E_{\text{ext}} + \frac{1}{2} \sum_{k, \ell = 1}^{N} \frac{Z_k Z_\ell}{|R_k - R_\ell|} \]  

(1.79)

is a function of \( \mathbf{X} \),

\[ E = E(\mathbf{X}) = E(R_{1,x}, R_{1,y}, R_{1,z}, R_{2,x}, R_{2,y}, R_{2,z}, \ldots, R_{M,x}, R_{M,y}, R_{M,z}) \]  

(1.80)

For the optimized structure \( \mathbf{X}' \), \( E \) has a minimum, and by expanding \( E \) to second order about the minimum (notice that first order derivatives are zero at the minimum) one finds

\[ E(\mathbf{X}) \approx E(\mathbf{X}') + \frac{1}{2} \sum_{k, \ell, u, v} \sum_{i, j, t} \left( \frac{\partial^2 E(\mathbf{X}')}{\partial R_{k,i} \partial R_{\ell,j}} \right) \times (R_{k,i} - R_{\ell,j}) (R_{\ell,j} - R_{\ell,t}) \]  

(1.81)

the series, in principal, may include the terms of higher order. Often the harmonic approximation turns out to be a reasonably good in some cases correction due to anharmonic ordered terms also have to be included in order to obtain an accurate description of the vibrational properties of the material of interest.

The matrix

\[ H = \begin{pmatrix} \frac{\partial^2 (\mathbf{X}')}{\partial R_{k,1,1} \partial R_{k,2,2}} \\ \end{pmatrix} \]  

(1.82)

is called hessian. For the optimized structure \( \mathbf{X}' \), the forces \( \frac{\partial E}{\partial R_{k,a}} \) vanishes. Actually there is also the case for saddle point, and in order to be absolutely sure that the optimized structure indeed belongs to a total energy-minimum one has require that all
eigenvalues of the Hessian matrix to be non-negative. Otherwise there would be a certain
linear combination of \((R_{i,j} - R_{k,l}^e)\) that would lead to a reduction of \(E\).

For some computational methods also the Hessian is calculated directly and analyti
cally. The first order derivative of \(E\) with respect to the nuclear coordinate, could be calculated
and observed that due to the fact what we do not solve the Schrödinger, Hartree-Fock or
Kohn-Sham equations exactly, but also approximately through application of the
variational method, we could not directly apply the Hellmann-Feynman theorem but had
to include additional contribution to the forces. The calculation of the second order
derivatives as needed for the Hessian is certainly not easier.

As an alternative one may first determine the structure of the total-energy minimum.
Subsequently, one may calculate the changes in the total energy when displacing the
various atoms slightly by considering more (many) different displacements. The results
of these calculations may finally may fitted with in an expression like Eq. (1.84).

Having written the total energy in the form of Eq. (1.84) can study vibrations. We will
then treat the nuclei as quantum particles and consider accordingly following nuclear
Hamilton operator:

\[
H_n = -\sum_{k=1}^{N} \frac{1}{2M_k} \nabla_k^2 + \frac{1}{2} \sum_{k,l=1}^{N} \sum_{i=1}^{2} \frac{\partial^2 E(X^e)}{\partial R_{k,i} \partial R_{l,j}} \times (R_{k,i} - R_{k,i}^e) (R_{l,j} - R_{l,j}^e) \tag{1.83}
\]

The eigenvalues and eigenfunctions to the Schrödinger equation

\[
H_n \Psi_n = E_n \Psi_n \tag{1.84}
\]

then define the energies and patterns (modes) of the vibrations of the system of interest.
In order to solve this equation it is of advantage to introduce the new coordinates

\[ u_k^* = \sqrt{M_k} (R_k^e - R_k^v) \]  

(1.85)

that are the derivation from the equilibrium position but scaled with the square root of the masses. The nuclear Hamilton operator of Eq (1.86) then takes the form

\[ H_n = -\sum_{k=1}^{M} \frac{1}{2} \frac{\partial^2 E(X^v)}{\partial R_{k_1,at} \partial R_{k_2,at}} u_{k_1,b_1} u_{k_2,a_2} \]  

(1.86)

As for the Hessian, this leads naturally to definition of matrix

\[ D = \left( \frac{1}{\sqrt{M_k, M_{k_2}}} \frac{\partial^2 E(X^v)}{\partial R_{k_1,at} \partial R_{k_2,at}} \right) \]  

(1.87)

which is the so-called dynamical matrix

Also in this case we should in principle solve the nuclear Schrödinger equation (1.87). The problem with this equation, however, is that all the different \( u \) mix, i.e., is a true 3M-dimensional problem. But if we diagonalize the dynamic matrix, write it as

\[ D = U^* \lambda U \]  

(1.88)

Where \( U \) is a unitary matrix and \( \lambda \) is a diagonal matrix containing the eigenvalues of \( D \), then we can define new coordinates

\[ U_i = \sum_{k=1}^{M} U_{ki} u_k \]  

(1.89)

Here, we simplify the notation by letting

\[ u_1 = u_{1,x} \]
\[ u_2 = u_{1,y} \]
These can be used in rewriting the nuclear Hamilton operator. First, we find for the kinetic energy part,

\[
\frac{\partial^2}{\partial u_i^2} = \frac{\partial}{\partial u_i} \left[ \sum_k \frac{\partial u_k}{\partial u_i} \frac{\partial}{\partial u_k} \right] \\
= \sum_k U_{ik} \sum_l \frac{\partial u_k}{\partial u_l} \frac{\partial^2}{\partial u_l \partial u_i}
\]

then

\[
-\frac{1}{2} \sum_i \frac{\partial^2}{\partial u_i^2} = -\frac{1}{2} \sum_{i,j} U_{ik} U_{ji} \frac{\partial^2}{\partial u_k \partial u_l} \\
= -\frac{1}{2} \sum_{k,l} \frac{\partial^2}{\partial u_k \partial u_l} \sum_{i,j} U_{ik} U_{ji} \\
= -\frac{1}{2} \sum_{i,j} \frac{\partial^2}{\partial u_k \partial u_l} \delta_{k,l} \\
= -\frac{1}{2} \sum_i \frac{\partial^2}{\partial u_i^2} \\
= -\frac{1}{2} \sum_i \frac{\partial^2}{\partial u_i^2}
\]  

Due to the unitarily of the matrix

Therefore, the nuclear Hamilton operator takes the form

\( u_{3M} = u_{M,Z} \) \hspace{1cm} (1.90)
\[ H_n = \sum_k \left[ -\frac{1}{2} \frac{\partial^2}{\partial u_i^2} + \frac{1}{2} \gamma_{kk} u_k^2 \right] \] (1.93)

\[ i.e., \text{there is no mixing between the different components (the different } k). \text{ In this form, it is straightforward to calculate the eigenvalues and eigenfuctions. To his end we observe that the form of the nuclear Hamilton operator in Eq (1.96) makes it possible to write the nuclear wavefunction as a product,} \]

\[ \Psi_n(R_1, R_2, ..., R_M) = \Psi_1(u_1) \Psi_2(u_2) \cdots \Psi_M(u_M) \] (1.94)

Interesting this into the nuclear Schrodinger equation gives 3M independent equations of the form

\[ \left[ -\frac{1}{2} \frac{\partial^2}{\partial u_i^2} + \frac{1}{2} \gamma_{kk} u_k^2 \right] \Psi_i(u_i) = E_k \Psi_i(u_i) \] (1.95)

the eigenvalues are then

\[ E_k = (m_k + \frac{1}{2}) \sqrt{\gamma_{kk}} \] (1.96)

where the integers \( m_k \) distinguish the different eigenvalues and eigenfuctions.

Thus \( m_k \) describes how the different atom move when the \( k \)th variational mode is excited and the eigenvalues \( \gamma_{kk} \) of the dynamically matrix are the square roots of the vibrations excitation energies.

There is one aspect that should be added, i.e. since we may translate or rotate the molecule without any energy cost, we will have 5 or 6 modes of zero energy, where 5 is valid for linear molecules and 6 for others.
1.5.1 Solid polymer electrolytes:

Compounds with the general formula CH$_3$O-(CH$_2$-CH$_2$-O)$_n$-CH$_3$ are known as glymes (glycol dimethyl ether). These homologues of Poly(ethylene oxide) (PEO) are liquids at room temperature. The use of PEO relies on its high chemical and thermal stability. These PEO polymer chain is highly flexible owing to the absence of unsaturation, i.e. it contains no double bonds, therefore can coordinate with various alkali-, alkaline-, transition- metal and lanthanide ions through the ether oxygen of PEO. The coordination strength of polyether has been expected to enhance by the multidentate nature and the flexibility of the polymer chain, which is responsible for several low energy conformations can be adopted depending on the cation coordination.

Poly(ethylene oxide) oligomers dissolve a variety of ionic salts such as LiCF$_3$SO$_3$ or Li(CF$_3$SO$_2$)$_2$N to form solid polymer electrolytes (SPE), exhibit high ionic conductivity, which facilitate their use in fuel cells, secondary batteries and other electrochemical devices. The ion-polymer and ion-ion interactions or ionic association in these systems are important in the ion transport phenomenon. Amongst these ionic association comprised of formation of ion-pairs or ion triplets, can be studied experimentally using the infrared and Raman spectroscopy. Interestingly the cation-polymer interactions result in the polymer segmental motion of the polymers. In order to understand the relationship between the ionic transport and local structure of the polymer matrix at the molecular level, ab initio quantum chemical calculations have been explored in the recent literature. The coordination of metal ion to ether oxygens of poly-ethers and the accompanying change in the chain conformation has consequently been of a great importance in understanding the transport properties of the electrolytes.
With this view a number of theoretical studies have been aimed to characterize the ion-polymer and ion-ion interactions in PEO oligomers bound by novel weakly coordinating salts.

1.5. 2 Ion-polymer and ion-ion interactions in Lithium Battery:

For a binary salt polymer electrolyte system wherein both anions and cations are mobile. To describe the system, three transport properties are required and these are usually conductivity, salt diffusion coefficient and transference number. Since there is only an electrode reaction for the lithium ions, salt concentration gradients build up. The transference number of the anion indicates how strong is the tendency for salt accumulation under the effect of the current while the diffusion coefficient indicates how rapidly the system is able to relax the salt concentrations. Figure 1 gives a schematic presentation of salt concentration polarization that occurs in membranes and composite electrodes. It can be seen that the concentration polarization leads to a limit on the thickness of the composite electrode that can be accessed. Transport properties also vary as function of salt concentration and location in the cell. For example, the composite cathode consists of polymer-salt filled with carbon black nano-particles (10-20% loading) and active cathode particles (1-10 μm). Consequently, the segmental motion of the polymer is inhibited in the regions close to the electrode surfaces leading to much different transport properties. Salt concentration gradients build up in the composite cathode and need time to relax between cycles. If salt diffusion coefficient is not high enough to allow the cell to relax, capacity fading occurs (1,2).
Fig. 1.1

One can also see that the concentration of salt next to the lithium electrode can increase to high levels. It has been shown that the Tg of polymer electrolytes increases as the salt concentration increases and consequently the conductivity decreases precipitously as the discharge proceeds. Figure 1.2 shows conductivity plots and plots of Tg of various polymers as a function of salt (LiTFSI) concentration. The polymer structure in this case is a comb branch structure with a polypropylene oxide backbone and side chains of varying lengths, which contain different ether groups. The ether groups are either ethylene oxide (EO) or trimethylene oxide (TMO). One can see a dramatic effect of the TMO groups on the Tg values as salt concentration increases and this affects conductivity at low temperatures, although there seems to be little effect at higher temperatures. However, the implication is clear that the TMO containing polymers will suffer much less than the ethylene oxide polymers from the effects of salt concentration.
Although the effects of concentration profiles may be alleviated by structural changes in polymer and salt, it is clear that the most attractive solution is to synthesize polyelectrolytes with a lithium transference number of one in order to completely avoid the salt concentration profiles. The comb branch structure appears to offer the best hope of achieving a polyelectrolyte with a satisfactory conductivity. It has been shown by modeling that a conductivity of 10^4 S/cm at 25°C.
will provide EV performance and this is the goal. The polyelectrolyte must not only possess good conductivity and hence have a low Tg but also must have sufficient mechanical strength to inhibit dendrite growth and be chemically stable to both lithium metal and metal oxides at 3.5-4.0 volts versus lithium. The polymer must also have sufficient flexibility to incorporate filler material such as carbon black, which will decrease the mobility of the polymer side chains. Figure 1.3 is a schematic representation of the polymer architecture that is envisioned as being ideal for the purpose. It consists of a cross-linked comb branch material with the anions (X') attached to the ends of the side chains and the side chains themselves may contain appropriate 4 solvating groups for lithium ions such as EO or TMO. The structure is very similar to that of fuel cell polyelectrolyte membranes and one can easily envision exchange of H⁺ for Li⁺.

1.6 Scope of present work:

In Chapter 2 we analyze the structure, charge distributions and vibrational characteristics of H₃CO-(CH₂CH₂O)₉CH₃—M (n=3-7) PEO oligomers by employing *ab-initio* and hybrid dneisty functional methods. Different rotamers for each member of the present series are generated by rotations around each C-C and C-O bonds of PEO backbone. The first part of the Chapter deals with the structure and stability of the different conformers of tri-to hepta- glymes. MESP topography has been explored to study the charge distribution and to find the binding site of the cation. In the second part the chapter focuses on the consequences of the cation coordination to the structure and vibrational spectra of the complex relative to the free PEO conformer. The binding energy has been calculated using the density functional method.
The local coordination of the mono- and divalent cations with different PEO oligomers and the consequent vibrational spectral changes has been discussed in Chapter 3. Thus the complexes of Na, K, Mg and Ca with the \( \text{CH}_3\text{-O-} (\text{CH}_2\text{-CH}_2\text{-O})_n \text{-CH}_3 \) \((n=2-7)\) as modeled systems, have been investigated. A comparison of cation-binding strengths with the ether oxygens of oligomer has been predicted by calculating the binding energy. The weakening of the carbon-oxygen bond in the oligomer-cation complex shows a downshift for C-O-C stretching vibration in the vibrational spectra, which can quantitatively be correlated with the strength of interactions.

In Chapter 4 the effect of the counter-anion viz. \( \text{BF}_4^- \), \( \text{ClO}_4^- \), \( \text{SCN}^- \) on the structure and vibrational spectra of \( \text{CH}_3\text{-} (\text{O-CH}_2\text{-CH}_2\text{-})_2 \text{-O-CH}_3 \) in the solid polymer electrolytes containing different alkali metal ions have been dealt with. The normal vibrations in these SPE have been analyzed in details. Characteristics vibrational frequency shifts to higher wavenumber (blue shift) and the lower wave number as well have been explained on the basis of electron density topography and the natural bond order analysis.

Chapter 5 presents the effect of the counter-anions, for example, \( \text{CF}_3\text{SO}_3^- \), \( \text{PF}_6^- \), \( (\text{CF}_3\text{SO}_2)_2 \text{N}^- \) on the structure and vibrational spectra of the SPE containing \( \text{CH}_3\text{-} (\text{O-CH}_2\text{-CH}_2\text{-})_2 \text{-O-CH}_3 \) and the alkali metal ion viz., Li+, Na+, K+ are discussed. Unlike presented in the preceding chapter the counter anions herein bring about a significant conformational change around the C-O bonds of diglyme in the 1:1:1 SPE. The normal vibrations in these have been analyzed. The molecular electroin density topography and the difference density in addition to the natural bond analysis have been utilized to rationalize the ‘frequency shift’ direction of the characteristics vibrations.
In Chapter 6 we investigate the suitability of an aromatic lithium bis(4-nitropheryl sulfanyl)imide, Li-N[SO₂(C₆H₅NO₂)]₂ (LiNPSI) salt as a plasticizer in the solid polymer electrolytes over the fluorine-rich LiTFSI. The binding patterns of NPSI with Li⁺ have been discussed in details. By calculating the ratio of charge to the volume enclosed by a given MESP isosurface, which encompasses the entire O₂S-N-SO₂ framework of the TFSI and NPSI anions, it has been inferred that the Li⁺ binds strongly to NPSI anion than TFSI⁻. Therefore, the observed lower ionic conductivities of the solid polymer electrolytes containing LiNPSI salts dissolved in PEO can be rationalized.
References:


50. Semi-empirical MO program MOPAC 2000, J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan


73. E. Fermi, Rend. Acad. Lincei 6, 602 (1927).


