Density functional Theory:
Theoretical Aspects
GENERAL

Density functional theory is tested on a large ensemble of model compounds containing a wide variety of functional group to understand better its ability to calculate molecular geometries, relative conformation energies, vibrational frequencies, dipole moment and net atomic charges. In this study, all density functional geometries were generated by local density functional self consistent calculation with gradient correction added in a perturbative fashion. Timings on scalar and vector architectures indicate that, for moderately sized systems, our density functional implementation requires only slightly less compiler resource than established Hartree Fock programe. While density functional (DF) theory is practically the only first principle, quantum mechanical approach in material science, physics and chemistry is dominated by ab inrtio (Hartree Fock correlated method) and semiempirical calculation.

2.1 Quantum Chemical Methods

Quantum chemical methods are described as quantitative and Qualitative. quantitative methods are ab-initio, semi-empirical and density functional. In ab-initio method the correct Hamiltonian for the system attempts a solution without the use of experimental data (other than molecular geometry). A Hartree-Fock SCF calculation seeks the antisymmetrized product of one electron functions that minimizes \( \int \psi \hat{H} \psi d\tau \), where \( \hat{H} \) is true Hamiltonian and is thus an ab-initio calculation. On the other hand semiempirical calculations use a simpler Hamiltonian than the correct molecular Hamiltonian and incorporate
Into the calculation experimental data e.g. atomic ionization potential that can be adjusted to fit experimental data whereas density functional (DF) is based on notion that the energy of an electronic system can be expressed in terms of its density. The theory and the analysis of calculated schemes, of quantum chemistry have been dealt with in details in a number of books\textsuperscript{(1-11)} and review articles\textsuperscript{(12-18)}.

Semi-empirical and ab-initio methods differ in the trade-off made between computational cost and accuracy of result. Semi-empirical calculations are relatively inexpensive and provide reasonable qualitative descriptions of molecular systems and fairly accurate quantitative predictions of energies and structures for systems where good parameter set exist. In contrast, ab-initio computations provide high quality quantitative predictions for broad range of systems. They are not limited to any specific class of system. Early ab-initio programs were quite limited in the size of system they could handle. Recent studies\textsuperscript{(19-31)} show that DFT is appearing as a better tool for calculating the ground state properties of molecules than the ab-initio methods used due to the fact that it is computationally less demanding for inclusion of electron correlation (comparable with HF methods and the semiempirical method).

2.2 Ab-initio (Non empirical) Method: The Hartree – Fock Method

Most methods are based on the single-particle approximation which is popularly known as MO picture that provides the basis for constructing the most important nonempirical methods of quantum chemistry.
2.2.1 Molecular Orbitals:

The MO approximation is based on the assumption that an individual spin orbitals \( \Psi \alpha \) or \( \Psi \beta \) (where \( \Psi \) is the function of space coordinates and \( \alpha (m_s = 1/2) \) or \( \beta (m_s = -1/2) \) are the functions of spin coordinates) corresponds to each electron. The full wave function of a many-electron system \( \Psi \) in the Hartree-Fock approximation is written as a Slater determinant whose form provides for the property of antisymmetry of \( \Psi \) required by the Pauli principle, with respect to the pairwise permutation of any electron.

\[
\psi(1, 2, \ldots n) = [n!]^{1/2} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \ldots & \varphi_n(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \varphi_1(2)\beta(2) & \ldots & \varphi_n(2)\beta(2) \\ \ldots & \ldots & \ldots & \ldots \\ \varphi_1(n)\alpha(n) & \varphi_1(n)\beta(n) & \ldots & \varphi_n(n)\beta(n) \end{vmatrix} \tag{1}
\]

This wave function defines \( n/2 \) molecular orbitals for a system with \( n \) electrons (closed shell). The determinant (1) is often referred to as a Slater determinant\(^{[32]}\).

2.2.2 Basis Set Expansions

The next approximation involves expressing the molecular orbitals as linear combination of a finite set of N prescribed one-electron functions known as basis function. These basis functions are usually centered on the atomic nuclei and so bear some resemblance to atomic orbitals. If the basis functions are \( \chi_1, \chi_2, \ldots, \chi_N \) then an individual orbital \( \Psi_i \) is written as:

\[
\Psi_i = \sum_{\mu=1}^{N} C_{\mu i} \chi_\mu \quad i = 1, 2, \ldots, N \tag{2}
\]
Where the coefficients $C_{nl}$ are known as the molecular orbital expansion coefficient. Two types of atomic basis functions have received widespread use.

### 2.2.2.1 Slater-type Atomic Orbitals (STOs)

STOs have exponential radial part. They are labelled like hydrogen atomic orbitals, 1s, 2s, 2p, ... and have the normalized form.

$$
\chi_{1s} = \left( \frac{e^3}{\pi} \right)^{1/2} \exp \left( -\xi_{1r} \right)
$$

$$
\chi_{2s} = \left( \frac{e^5}{96\pi} \right)^{1/2} r \exp \left( -\xi_{2r} \frac{r}{2} \right)
$$

(3)

$$
\chi_{2p} = \left( \frac{e^5}{32\pi} \right)^{1/2} r \exp \left( -\xi_{2r} \frac{r}{2} \right)
$$

Where $\xi_1$ and $\xi_2$ are constants determining the size of the orbitals. STOs provide reasonable representations of atomic orbitals with standard $\xi$ values recommended by Slater\textsuperscript{33}. These are, however, not well suited to numerical work, and use in practical molecular orbital calculations has been limited. Clementi and Roetti\textsuperscript{34} performed analytic Hartree-Fock calculations for the ground and excited states of the first 54 elements of the periodic table. Electron densities calculated from Hartree-Fock wave functions are quite accurate. The Hartree-Fock electron probability density gives an atomic radius in good agreement with the empirically determined Van der Waals radius\textsuperscript{35}. The minimal basis set of Slater type orbitals include only those STOs that correspond to occupied AOs in the separated atom limit. The minimal basis set can be improved by adding additional STOs to various nuclei.
2.2.2.2 Gaussian-type Atomic Orbitals (GTOs):

These are powers of x, y, z multiplied by exp (- αr²), α being a constant determining the size, that is radial extent, of the function. In normalized form, three representative Gaussian functions are:

\[ g_s(α, r) = \left( \frac{2α}{π} \right)^{3/4} \exp(-αr^2) \]

\[ g_y(α, r) = \left( \frac{128α^3}{π^3} \right)^{1/4} y \exp(-αr^2) \quad (4) \]

\[ g_{xy}(α, r) = \left( \frac{2048α^5}{π^5} \right)^{1/4} xy \exp(-αr^2) \]

The Gaussian functions \( g_s, g_x, g_y, \) and \( g_z \) have angular symmetries of the s- and three p - type atomic orbitals. The six second-order functions \( g_{xx}, g_{yy}, g_{zz}, g_{xy}, g_{xz}, g_{yz}, \) do not have angular symmetry of atomic orbitals. However, they may be combined to give a set of d-type functions.

Gaussian-type functions were introduced into molecular orbital computations by Boys\(^{(36)}\). These are less satisfactory than STOs as representation of atomic orbitals, particularly because these do not have a cusp at origin. Nevertheless, these have the important advantage that all integral in the computations can be evaluated explicitly without recourse to numerical integration,

2.2.2.3 Double \( \xi \) Basis Set

Here every minimal basis AO is represented by an "inner-outer" pair of STOs. A further extension can be made by adding further STOs with symmetries different from those present in the minimal basis. Functions of this sort are called polarization functions. For molecules
with no atom heavier than fluorine, only, 1s, 2s and 2p AOs are involved
and these have the form:

\[ \chi_{1s}(\xi_1, r) = \left(\frac{\xi_1}{\pi}\right)^{\frac{1}{2}} \exp(-\xi_1 r) \]

\[ \chi_{2s}(\xi_2, r) = \left(\frac{\xi_2}{3\pi}\right)^{\frac{1}{2}} r \exp(-\xi_2 r) \] (5)

\[ \chi_{2p}(\xi_2, r) = \left(\frac{\xi_2}{\pi}\right)^{\frac{1}{2}} r \exp(-\xi_2 r) \cos \theta \]

Variational calculation of LCAO-MO molecular orbitals using basis
sets (5) with fixed \( \xi \) exponents have been published for a number of
molecules\(^{37-43}\). These involve the use of somewhat arbitrarily chosen
standard sets of \( \xi \) values but it is preferable to treat exponents as
parameters leading to final optimized values.

But full Slater type calculations are time consuming and so each
STO is replaced by a linear combination of Gaussian type orbitals. The
reason is that in SCF calculation, one must calculate of the order of
\( K^{41/8} \) two-electron integral which are very difficult and time consuming
with STOs. But for 1s Gaussians, the four- centre integral reduces to
two-centre integral which can be calculated rapidly and efficiently with
Gaussian functions.

A technique of this sort was first used by Foster and Boys\(^{38}\) and
discussed in some detail by Reeves, Fletcher, O-Ohata, Takata and
Huzinaga\(^{44}\), who proposed obtaining the Gaussian representations by
least squares fitting. In calculations of this sort, the STOs are replaced
by a finite Gaussian expansion at all points in the calculation. The
results approach those of the full Slater-type calculations as the size of
the Gaussian set increases.
The Slater type orbitals are represented using 2-6 Gaussians\textsuperscript{[44]} functions (referred to as STO-2G, STO-3G, STO-4G, STO-5G and STO-6G) and the approach of LCAO-SCF calculations towards the full Slater type results have been studied.

2.2.2.4 Contracted Gaussian Functions:

A linear combination of Guassians function as basis is called a contracted Gaussian functions e.g

\[ \chi_{\mu}^{CIF} = \sum_{\nu=1}^{I} d_{\mu\nu} \chi_{\nu}(\alpha, \beta, r) \]  

(6)

Where \( d_{\mu\nu} \) = Contraction coefficients are fixed within a given basis set. \( \alpha_{\nu} \) = Contraction exponent.

L = Length of contraction

The individual \( g \) being termed as primitive Gaussian.

Thus we have

\[ \varphi_{\ell} = \sum_{\mu} C_{\mu\ell} \chi_{\mu} = \sum_{\mu} C_{\mu} \left( \sum_{\nu=1}^{I} d_{\mu\nu} \chi_{\nu}(\alpha, \beta, r) \right) \]  

(7)

A common way of determining contraction is from the results of atomic SCF calculations. Here, one uses a relatively large basis of uncontracted Gaussian, optimizes all exponents and determines the SCF coefficients of each of the derived AOs. The optimized exponents and SCF coefficients can then be used to derive suitable contraction exponents \( \alpha \) and coefficients \( d_{\mu\nu} \) for a smaller basis set in subsequent molecular calculations.

In the method, each Slater type atomic orbital is replaced by an \( \text{AO}\chi' \) which is the sum of K Gaussian-type orbitals (K = 2-6). These
combinations are obtained for STOs with \( \xi = 1 \) and then uniformly scaled. Thus

\[
\chi(\xi, r) = \xi^{3/2} \chi'(1, \xi r)
\]

(8)

where \( \chi' \text{ nl}(\xi = 1, r) = \sum_k d_{nl,k} g_k(\alpha_n, k, r) \)

(9)

where the subscripts \( n \) and \( l \) define the specific principal and angular quantum numbers e.g., \( \chi_{1s} \) and \( g_1 \) are normalized Gaussian functions.

The 2s, 3s, 4s, and 5s exponential functions are replaced by a linear combination of 1s Gaussian function. This leads to considerable saving of integral evaluation time. Secondly, the expansion for atomic functions of given principal quantum number \( n \) share a common set of Gaussian exponents.

The values of Gaussian exponents, \( \alpha \) and the linear expansion coefficients, \( d \), have been determined by minimizing, in a least square sense, the error in the fit of the Gaussian expansion to the exact Slater orbital.

\[
e_{nl} = \int (\chi_{nl}^{\text{Slater}} - \chi_{nl}^{\text{Gaussian expansion}})^2 d\tau
\]

(10)

Minimization is performed simultaneously for all expansions of a given \( n \) quantum numbers e.g. 2s and 2p Gaussian expansions are obtained by minimization of sum integrals.

\[
e_{2s} + e_{2p} = \int (\chi_{2s}^{\text{Slater}} - \chi_{2s}^{\text{Gaussian expansion}})^2 d\tau + \int (\chi_{2p}^{\text{Slater}} - \chi_{2p}^{\text{Gaussian expansion}})^2 d\tau
\]

(11)

Values for \( \alpha \) and \( d \) for expansion lengths \( K \) between 2 and 6 along with the least squares error are tabulated in the original literature\(^{45,46}\).
Once we have contracted Gaussian function corresponding to each STO. We have minimal basis set, double-$\xi$ basis set, double-$\xi$, plus polarization functions etc. Typically, ab-initio calculations involve any where from (1-7) primitive Gaussian functions for each contracted Gaussian function.

2.2.2.5 Minimal Basis Set: STO-3G:

The simplest level of basis is minimal\cite{45,46} and corresponds to one basis function per AO. So it has the least number of functions per atom required to describe the occupied AOs of that atom. It is relatively inexpensive but since the minimal basis set is too small, it is relatively inaccurate. This is because one considers 1s, 2s and 2p i.e. five functions to constitute a minimal basis set for Li and Be even through the 2p orbital is not occupied in these atoms.

The 2sp (2s and 2p), 3sp, 4sp, 3d...etc. shells are considered together. So the minimal basis consists of one function for H & He, 5 functions for Li to Ne, 9 functions for Na to Ar etc. Because of the small number of functions in a minimal basis set these functions should be of near optimum form. One would prefer to use Slater function or functions that closely resemble the known shape of AOs. The STO-LG method uses a contraction of L primitive Gaussians for each basis function, where the contraction coefficient and exponents are chosen so that the basis functions approximate Slater functions.

The general STO-LG procedure uses contraction lengths upto $L = 6$. The longer the length of contraction, the more time is spent in integral evaluation. It has been empirically determined that a contraction of
length 3 is sufficient to lead to calculated properties that reproduce essentially all the valence features of a Slater calculation and **STO-3G** has become the standard for minimal basis calculations.

**2.2.2.6 Split Valence Basis Set:**

A minimal basis set has rather limited variational flexibility particularly if the exponents are not optimized. The first step in improving upon the minimal basis set is using a double-zeta basis set.

In the split valence basis sets one is not concerned with achieving a very accurate description of the inner shells of the first-row atoms. However, to allow for anisotropy in the valence shell, it is necessary to split the valence atomic orbitals into two parts.

In particular\(^{47}\), a series of basis sets have been defined and designated K-LMG where K, L & M are integers. Such a basis for a first row elements (Li to Ne), consists of s-type inner-shell function with K Gaussians, an inner set of valence s and p functions with L Gaussians and another outer sp set with M Gaussians.

**Larger Split-valence: 4-31G, 5-31G & 6-31G basis Set:**

The original\(^{47}\) 4-31G, 5-31G and 6-31G split valence basis sets were obtained by optimizing all Gaussians exponents and contraction coefficients. Ideally, the valence part of a split-valence basis should be determined with a very good inner shell function. This is because the 'falling inward' of the valence functions towards the nucleus is undesirable.

The 4-31G basis set is defined for H & B, C,N,O,F and has wide spread applications\(^{48,49}\). Here, only the valence functions are double\(^{50}\) and a single function is still used for each inner shell orbital. Not
splitting the inner shell functions has some effect on the total energy but little effect on dipole moments, valence ionization potentials, charge densities etc. The 4-31G acronym implies that the valence basis functions are contractions of three primitive Gaussians (the inner functions) and one primitive Gaussian (the outer function), whereas the inner shell functions are contractions of four primitive Gaussians.

The 4-31G basis set has 2 functions for H & He, 9 functions for Li to Ne, 13 functions for Na to Ar etc.

In the 4-31G basis set, each inner shell atomic orbital is represented by a single function, which in turn is written in terms of 4 primitive Gaussian i.e. Eq. (12) with $K = 4$

$$\chi_{n\ell}(r) = \sum_{k=1}^{K} d_{n\ell,k} (\alpha_{n,k}, r)$$ (12)

The contracted and diffuse basis functions representing valence-shell orbital are written in terms of Eq. (13) & (14) with expansion lengths $K'$ & $K''$ chosen as 3 & 1 respectively.

$$\chi'_{n\ell}(r) = \sum_{k=1}^{K'} d'_{n\ell,k} (\alpha'_{n,k}, r)$$ (13)

$$\chi''_{n\ell}(r) = \sum_{k=1}^{K''} d''_{n\ell,k} (\alpha''_{n,k}, r)$$ (14)

For heavy atom we choose $K = 4$, $K' = 3$, $K'' = 1$

As in STO-3G basis, the $2s$ & $2p$ functions share the exponents. Here the exponents and contraction coefficients were varied until the energy of atomic SCF calculation reached a minimum.

The 5-31G and 6-31G are two larger basis sets\(^{[51]}\). They are developed in a similar manner like 4-31G but with an improved inner
shell description. The number of Gaussian functions in the valence shell is unaltered. The extended basis sets are specified as follows:

5-31G: For heavy atoms, $K = 5$, $K' = 3$, $K'' = 1$ and for H, $K' = 3$, $K'' = 1$.  
6-31G: For heavy atoms, $K = 6$, $K' = 3$, $K'' = 1$ and for H, $K' = 3$, $K'' = 1$.

(b) **Split Valence 3-21G and 6-21G Basis Set:**

A best 21G valence part of a split valence K-2IG basis\(^{52}\) is one in which all parameters are optimized with $K$ large e.g, 6-21G. But due to computational inefficiency the inner shell basis functions are replaced by one with smaller $K$ without reoptimizing the valence functions.

**2.2.3 Variational Method and Hartree-Fock Theory:**

Hartree-Fock theory is based on the variational method in quantum mechanics. According to variational principle, the energy of the exact wavefunction $(E)$ serves as a lower bound to the energy $(E')$ calculated by any other normalized antisymmetric function. The best single determinant wave function, in an energy sense, is found by minimizing $E'$ w.r.t the coefficients $C_{\mu i}$. This implies the variational equations

$$\frac{\partial E'}{\partial C_{\mu i}} = 0 \quad \text{(all } \mu, i)$$  \hspace{1cm} (15)

**2.2.3.1 Closed-Shell Systems:**

The variational condition (15) leads to a set of algebraic equation for $C_{\mu i}$. These were derived independently for the closed-shell wavefunction (1) by Roothaan\(^{53}\) and by Hall\(^{54}\). The Roothaan-Hall equations are
\( \sum_{\nu=1}^{N} \left( F_{\nu \nu} - \varepsilon \delta S_{\nu \nu} \right) C_{\nu \nu} = 0 \mu = 1, 2, \ldots, N \) \hfill (16)

with the normalization conditions

\( \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} C_{\mu \nu}^* S_{\mu \nu} C_{\nu \nu} = 1 \) \hfill (17)

Here, \( \varepsilon \) is the one electron energy of \( \psi \), \( S_{\mu \nu} \) are the elements of \( N \times N \) overlap matrix.

\( S_{\mu \nu} = \int \chi_{\mu}^*(l) \chi_{\nu}(l) \, dx_1 \, dy_1 \, dz_1 \) \hfill (18)

and \( F_{\mu \nu} \) are the elements of another \( N \times N \) matrix, the Fock matrix,

\( F_{\mu \nu} = H_{\mu \nu}^{\text{core}} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} P_{\lambda \sigma} \left( \mu \nu | \nu \sigma \right) - \frac{1}{2} \left( \mu \lambda | \nu \sigma \right) \) \hfill (19)

Where \( H_{\mu \nu}^{\text{core}} \) is a matrix representing the energy of a single electron in the field of "Bare" nuclei. Its elements are

\( H_{\mu \nu}^{\text{core}} = \int \chi_{\mu}^*(l) H(l) \chi_{\nu}(l) \, dx_1 \, dy_1 \, dz_1 \)

and \( H_{\mu \nu}^{\text{core}}(l) = -\frac{1}{2} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) - \sum_{A=1}^{N} \frac{Z_A}{r_{1A}} \) \hfill (20)

Here \( Z_A \) is the atomic number of atom \( A \) and summation is carried out over all atoms. The quantities \( (\mu \nu | \lambda \sigma) \) appearing in (19) are two electron repulsion integrals:

\[ (\mu \nu | \lambda \sigma) = \int \chi_{\mu}^*(l) \chi_{\nu}(l) \left( \frac{1}{r_{12}} \right) \chi_{\lambda}^*(l) \chi_{\sigma}(l) \, dx_1 \, dy_1 \, dz_1 \, dx_2 \, dy_2 \, dz_2 \] \hfill (21)

\( P_{\lambda \sigma} \) are the elements of the one electron density matrix.

\( P_{\lambda \sigma} = 2 \sum_{\nu=1}^{\text{occ}} C_{\lambda \nu}^* C_{\sigma \nu} \) \hfill (22)

The electronic energy, \( E_{\text{el}} \) is given by
\[ E_{\text{el}} = \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} P_{\mu \nu} \left( F_{\mu \nu} + H_{\mu \nu}^{\text{core}} \right) \]  

(23)

The total energy is obtained by adding \( E_{\text{el}} \) to the energy accounting for the internuclear repulsion

\[ E_{\text{tot}} = E_{\text{el}} + \sum_{A \neq B}^{M} \sum \frac{Z_{A}Z_{B}}{R_{AB}} \]  

(24)

The Roothaan-Hall equations (16) are not linear since the Fock matrix \( F_{\mu \nu} \) depends on the molecular orbital coefficients \( C_{\mu i} \) through density matrix expression Eq. (22), solution involves an iterative process. Since the resulting MOs are derived from their own effective potential, the technique is frequently called self-consistent-field (SCF) theory.

2.2.3.2 Open Shell Methods

For open shell systems, an unrestricted method\(^{(47)}\) capable of treating unpaired electrons needed. For this case the alpha and beta electrons are in different orbitals, resulting in two sets of molecular orbital expansion coefficients:

\[ \phi_{i}^{\alpha} = \sum_{\mu} C_{\mu i}^{\alpha} \chi_{\mu} \quad \text{and} \quad \phi_{i}^{\beta} = \sum_{\mu} C_{\mu i}^{\beta} \chi_{\mu} \]

The two sets of coefficients result in two sets of Fock matrices and their associated density matrices, and ultimately to a solution producing two sets of orbitals. These separate orbitals produce proper dissociation to separate atoms, correct de localized orbitals for resonant systems and other attributes characteristics of open shell systems. However, the eigen functions are not pure spin states, but contain some amount of spin contamination from higher states.
2.2.4 Post-SCF Methods:

Hatree-Fock theory provides an inadequate treatment of the correlation between the motions of the electrons within a molecular system especially that arising between electrons of opposite spin. Any method which goes beyond SCF in attempting to treat electron correlation is known as a post-SCF method.

In order to account for the energy of electron correlation, the following two procedures are currently used:

(a) The method of configuration interaction (CI) and

(b) The method of perturbation theory of Moller-Plesset (MP).

2.2.4.1 Configuration Interaction (CI)

Configuration Interaction (CI) methods begin by noting that the exact wavefunction $\Psi$ can not be expressed as a single determinant, as Hartree-Fock theory assumes. CI proceeds by constructing other determinants by replacing one or more occupied orbitals within the Hartree-Fock determinants with a virtual orbital.

In a single substitution, a virtual orbital, say $\chi_b$ replaces an occupied orbital $\chi_i$ within the determinant. This is equivalent to exciting an electron to a higher energy orbital. Similarly, in a double substitution two occupied orbitals are replaced by virtual orbitals: $\chi_a \rightarrow \chi_i$ and $\chi_b \rightarrow \chi_j$. Triple substitution would exchange three orbitals and so on.
(a) Full CI

The full CI method forms the wavefunction $\Psi$ as a linear combination of the Hartree-Fock determinant and all possible substituted determinants:

$$\Psi = a_0 \psi + \sum_{s>0} a_s \psi_s,$$

Where the summation $\sum$ is over all substituted determinants. The unknown coefficient $a_s$ are determined by minimizing the energy of the resultant wavefunction (linear variational method)

$$\sum_s (H_{ss} - E_i \delta_{ss}) a_s = 0 \quad i = 0, 1, 2, \ldots \quad (25)$$

Here $H_{st}$ is configurational matrix element

$$H_{st} = \int \ldots \int \psi^*_s \hat{H} \psi_t \, d\tau_1 d\tau_2 \ldots d\tau_n \quad (26)$$

and $E_i$ is an energy.

The lowest root $E$ of Eq. (25) leads to the energy of the ground state. From Eq. (26), $H_{00}$ is the Hartree-Fock energy. If $s$ is a single substitution, $H_{0s}$ vanishes by Brillouin's theorem\(^{(65)}\). If $s$ is a substitution which is triple or higher, $H_{0s}$ again vanishes, due to the fact that the, hamiltonian contains only one -and two -electron terms. It is only the double substitutions which lead to nonvanishing $H_{0s}$. As a result, the simplest correlation models account only for determinants formed by double substitutions,

(b) Limited CI

Full CI results are not practical for many-electron systems with large basis sets. To turn the full CI equations into practical equations
that can be solved is to limit the length of CI expansion by truncating the CI expansion at some level of substitution\(^{56}\)

Inclusion of single substitution functions only termed configuration Interaction, Singles or CIS

\[
\psi_{\text{CIS}} = \psi_0 + \sum \sum a_i^* \psi_i^* \tag{27}
\]

normally leads to no improvement relative to Hartree-Fock wavefunction energy. If Double substitution functions are included then it is termed configuration Interaction, Doubles or CID.

\[
\psi_{\text{CID}} = \psi_0 + \sum \sum \sum a_{ab} \psi_{ab} \tag{28}
\]

At a slightly higher of theory in CISD both single & double substitution are added

\[
\Psi_{\text{CISD}} = \psi_0 + \sum \sum a_i^* \psi_i^* + \sum \sum a_{ab} \psi_{ab} \tag{29}
\]

CISD suffers from a serious deficiency that it is not size-consistent\(^{57}\). A correction is applied to CISD energies to correct for this problem\(^{58,59}\). However due to the approximate nature of such corrections and the efficient formulation of exactly size-consistent schemes, CISD etc are no longer the methods of choice in quantum chemical application.

### 2.2.4.2 Moller-Plesset Theory:

Moller and Plesset Theory\(^{60}\), closely related to many-body perturbation theory, treats the electron correlation as a perturbation on the Hartree-Fock problem. Moller-Plesset models are formulated by introducing a generalized electronic Hamiltonian, \(\hat{H}_\lambda\) as
\[ \hat{H} \lambda = \hat{H}_0 + \lambda \hat{V} \]  

(30)

Here, \( \hat{H}_0 \) is an operator such that the matrix with elements

\[ \int_\cdots \int \psi_i \hat{H}_0 \psi_j \, d\tau_1 \, d\tau_2 \ldots \, d\tau_n \]

is diagonal. The perturbation, \( \lambda \hat{V} \) is defined by

\[ \lambda \hat{V} = \lambda (\hat{H} - \hat{H}_0) \]  

(31)

Where \( \hat{H} \) is the correct Hamiltonian and \( \lambda \) is a dimensionless parameters. In MP theory, the zero order Hamiltonian, \( \hat{H}_0 \), is taken to be the sum of the one-electron Fock operator. The eigen value, \( E_s \) corresponding to a particular determinant, \( \Psi_s \) is the sum of the one-electron energies. \( \varepsilon_i \) for the spin orbitals which are occupied in \( \Psi_s \).

\( \Psi_\lambda \) and \( E_\lambda \) the exact or full CI (with in a given basis set) ground-state wavefunction and energy for a system described by the hamiltonian \( \Delta_\lambda \), which can be expanded in powers of \( \lambda \) according to Rayleigh-Schroedinger perturbation theory\(^{[61]}\).

\[ \Psi_\lambda = \Psi^0 + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots . \]

\[ E_\lambda = E^0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots . \]  

(32)

Correlation methods can be formulated by setting the parameter \( \lambda = 1 \), and by truncation of the series in Eq. (32) to various orders. We refer truncation after second order as MP2, after third-order as MP3 and so forth. The Moller-Plesset energy to first order is Hartree-Fock energy. The first-order contribution to the wavefunction is

\[ \psi^{(1)} = \sum_{s \neq 0} (E_0 - E_s)^{-1} V_{s0} \psi_s \]  

(33)

Where \( V_{s0} \) are matrix elements involving the perturbation operator, \( \hat{V} \).
\[ \int \cdots \int \psi^* \hat{V} \psi_0 \, d\tau_1 \, d\tau_2 \ldots \, d\tau_n \]

It follows that the first-order contribution to the coefficient \( a_s \) Eq. (25) is given by

\[ a_s^{(1)} = (E_0 - E_s)^{-1} V_{s0} \]

The second-order contribution to the Møller-Plesset energy is

\[ E^{(2)} = -\sum_{ij} (E_0 - E_s)^{-3} |V_{s0}|^2 \]

(34)

Where \( \sum \) indicates that summation is to be carried out over all double substitutions. If \( \Psi_s \) is the double substitution \( ij \to ab \), the explicit expression for \( V_{s0} \) is

\[ V_{s0} = (ij \parallel ab) \]

Where \( (ij \parallel ab) \) is a two electron integral over spin orbitals, defined by

\[ (ij \parallel ab) = \int \left[ \chi_i^*(1) \chi_j^*(2) \left( \frac{1}{r_{12}} \right) \chi_a(1) \chi_b(2) - \chi_i(1) \chi_a(2) \right] d\tau_1 d\tau_2 \]

(35)

The second-order contribution to the energy then becomes

\[ E^{(2)} = -\sum_{a \neq c} \sum_{i \neq j} \sum_{a \neq b} \sum_{c \neq a} (E_{a} + E_{b} - E_{i} - E_{j}) \left| (ij \parallel ab) \right|^2 \]

(36)

The third-order contribution to the Møller-Plesset energy also follows directly from Rayleigh-Schrödinger theory, it is

\[ E^{(3)} = \sum_{a} \sum_{i} (E_0 - E_s)^{-1} (E_0 - E_i)^{-1} V_{0a} (V_{ai} - V_{00} \partial_{a}) V_{10} \]

(37)

The matrix element \( V_{st} \) between different double substitutions require a full integral transformation or other techniques of comparable complexity\(^{57,62,63}\).
2.3 Density Functional Theory: The Development of Function

Density functional theory is principally a theory of an atomic or molecular electronic ground state\(^{64,65}\). The System has \(N\) electrons and a fixed set of nuclear positions, the nuclei give rise to an external potential, \(V(r)\), in which the, electrons move and repel each other, The wavefunction is determined by \(N\) and \(V\), as is the electronic energy: \(E[N,V]\). The electron density \(\rho(r)\) is \(N\) times the integral at the square of the wavefunction over all electronic space and spin coordinates except the space coordinates of one. The density determines \(V(r)\) and \(N\) uniquely. Hence, \(E[N,Y] = E[\rho]\)

The total electronic energy is given by

\[
E[\rho] = F[\rho] + \int V(r) \rho(r) \, dr \tag{38}
\]

Where the functional \(F[\rho]\), a universal function of \(\rho\), is the sum of the kinetic energy functional \(T[\rho]\) and the electron electron repulsion functional \(V_{ee}[\rho]\). The variational principle determining the density is

\[
\delta \left\{ E[\rho] - \mu N[\rho] \right\} = 0 \tag{39}
\]

where \(\mu\) is a Lagrange multiplier for normalization of \(\rho\) such that,

\[
\int \rho(r)dr = N(\rho) = N
\]

otherwise

\[
\mu = V(r) + \frac{\delta F[\rho]}{\delta \rho(r)} = \text{constant} \tag{40}
\]

The quantity \(\mu\) is the chemical potential of the system. Differentiats for any change from one ground state to another are given by

\[
dE = \mu dN + \int \rho(r)dV(r)dr \tag{41}
\]
and

\[ d\mu = \eta dN + \int f(r) dV(r) dr \]  \hspace{1cm} (42)

\( \mu, \eta \) and \( f(r) \) are of considerable chemical importance. \( \mu \) is the negative of the absolute electro negativity\(^{(66)} \), \( \eta \) is the absolute chemical hardness\(^{(67)} \), and \( f(r) \) is the Fukui function or reactivity index\(^{(68)} \).

### 2.3.1 Development of Functional:

The homogeneous electron gas has been particularly instrumental\(^{(76,77)} \) in fostering useful approximate expressions for the exchange-correlation energy. The exchange correlation energy for the homogeneous electron gas can be written as:

\[ E_{xc} = E_x + E_c \]  \hspace{1cm} (43)

The representation of the exchange correlation energy by Eq. (43) has been coined\(^{(76)} \) as local density approximation (LDA),

(a) Exchange Functionals

(b) Correlation functionals

(c) Hybrid Functionals

**(a) Exchange Functionals** - Two types of exchange functionals available are:

(i) Slater (Xa) Functional: - The simplest exchange functional is the Slater (Xa) functional. Hartree -Fock exchange energy of an inhomogeneous many -electron system can be approximated as LDA

\[ E_x^{\text{LDA}} = -\frac{9}{4} \alpha \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} \sum_\sigma \int \rho_\sigma^{\frac{2}{3}} d^3r \]  \hspace{1cm} (44)
where the constant $\alpha$ is taken as a parameter and a either "up" or "down" electron spin, and where the integrand is essentially the volume exchange-energy density of a uniform spin-polarized electron gas of spin density $\rho_\sigma$. The exchange scaling factor $\alpha$ is 0.7

$$V_\xi = \frac{\partial E_{\xi}^{1/4}}{\partial \rho_\sigma(r)} = -3\alpha \left( \frac{3}{4\pi} \right)^{1/3} \rho_\sigma$$

(ii) **Becke 88 Exchange Functional:**

Exchange-energy corrections depending on local density gradients (LDG) by Sham$^{(78)}$ and nonlocal corrections of weighted density scheme by Gunnarsson and Jones$^{(79)}$ were proposed but gradient-type correction have received most attention due to their great simplicity.

The exact asymptotic behaviour of the exchange-energy density of any finite many-electron system is known, and is given by:

$$\lim_{r \to \infty} U^\sigma_\xi = -\frac{1}{r}$$  \hspace{1cm} (45)

where $U^\sigma_\xi$ is the coulomb potential of exchange charge or Fermi hole density $\rho_\xi^\sigma(r,r')$ at reference point$^{(80)}$ and is related to the total exchange energy by:

$$E_x = \left( \frac{1}{2} \right) \sum_\sigma \int \rho_\sigma U^\sigma_\xi d^3r$$  \hspace{1cm} (46)

This result reflects fact that, for reference points very far from finite system, the Fermi hole remains "attached" to the system.

The asymptotic behaviour of the spin density $\rho_\sigma$ is also known$^{(81)}$

$$\lim_{r \to \infty} \rho_\sigma e^{-a \sigma r}$$  \hspace{1cm} (47)

where $a$ is a constant related to the ionization potential of the system.

51
In view of this known asymptotic density dependence, Becke\(^{82}\) proposed a gradient-corrected exchange-energy functional that reproduces the exact asymptotic behaviour of Eq. (45) and (46).

\[
E_x = E_x^{1/34} - \beta \sum \rho^{4/3}_\sigma \frac{x^2_\sigma}{\left(1 + 6\beta \sigma \sinh^{-1} x^\gamma_\sigma\right)} \, d^3r
\]  \hspace{1cm} (48)

where \(\beta\) is a constant. This functional reduces to the LGC expression in the limit of small density gradients and function \(\sinh^{-1} (x\sigma)\) is expressible as a Taylor series in even powers of \(x\sigma\) as required of any analytically well-behaved functional.

This functional contains only one parameter \(\beta\) because the coefficients of \(x_\sigma\), \(\sinh^{-1} x_\sigma\) is fixed by Eq. (45). Parameter \(\beta\) is determined by a least squares fit to exact atomic Hartree-Fock data. The best-fit value of \(\beta\) is 0.0042 a.u. This one-parameter functional fits atomic Hartree-Fock exchange energies better than two-parameter functional of Becke\(^{83,84}\).

(b) **Correlation Functional**: 

Various types of local and gradient corrected correlation functional are available.

(i) **Vosko, Wilk and Nusair (VWN) Functional**:

Vosko, et al., made a careful analysis of the spin dependence of the Random Phase Approximation (RPA) of the uniform electron gas and proposed the more accurate description of RPA\(^{85}\), which is accurate to better than 10% for the standard variables \(r_s\) and \(\xi\) for density and spin polarization respectively. The new RPA results were combined with Ceperley and Alder's calculation by means of two-point Pade
approximant interpolation formula to produce a new \( \varepsilon_c (r_s, \xi) \) that is
accurate for the important densities in atoms, molecules and solids, and
thus provide a reliable means for judging the validity of LSDA.

\[
E_c = \int \rho \varepsilon_c (r_s, \xi) d^3r
\]

Where \( \rho = \rho_\alpha + \rho_\beta \) \( r_s = \left( \frac{3}{4\pi \rho} \right)^{1/3} \) and \( \xi = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta} \)

The correlation potential used is

\[
\varepsilon_c (r_s, \xi) = \varepsilon^p_c (r_s) + \varepsilon^t_c (r_s) g(\xi) x \left( 1 + \frac{4}{g(2^{1/3} - 1)} \frac{\varepsilon^p_c (r_s) - \varepsilon^t_c (r_s)}{\varepsilon^t_c (r_s)} - 1 \right) \xi^4 \right) \tag{49}
\]

where \( g(\xi) = \frac{9}{8} \left( 1 + \xi \right)^{4/3} + \left( 1 - \xi \right)^{4/3} - 2 \]

P & F stand for para/ferro states respectively and various \( \varepsilon_c \) have the form

\[
\varepsilon_c (r_s) = A \left\{ \ln \frac{x^2}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x+b} - \frac{bx_0}{X(x_0)} \left[ \ln \frac{(x-x_0)^2}{X(x)} + 2 \frac{(b+2x_0)}{Q} \tan^{-1} \frac{Q}{b+2x_0} \right] \right\} \tag{50}
\]

Where \( X(x) = x^2 + bx + c \), \n\( Q = (4c - b^2)^{1/2} \)

For \( \varepsilon^p_c (r_s) \), \( A = 0.0621814, X_0 = 0.409286, B = 13.0720 \)

and \( c = 42.7198 \); for \( \varepsilon^t_c (r_s) \) \( A = v_1 (0.0621814) \)

where \( x_0 = -0.743294, b = 20.1231, c = 101.578 \)

These formulas are generally accepted as the most accurate
available for uniform gas correlation per particle. Introducing

\[
h (r_s) = \frac{4}{g(2^{1/3} - 1)} \frac{\varepsilon^p_c (r_s) - \varepsilon^t_c (r_s)}{\varepsilon^t_c (\xi)} - 1 \tag{51}
\]

The derivatives are expressible as

\[
\frac{\partial E_c}{\partial \rho_i} = \varepsilon_c (r_s, \xi) + \rho \frac{\partial \varepsilon_c (r_s, \xi)}{\partial \rho_i}, \quad i = \alpha, \beta \tag{52}
\]
\[
\rho \frac{\partial \varepsilon_c(r_s, \xi)}{\partial \rho} = \frac{x}{6\rho} \left[ \varepsilon''_c(r_s) + \varepsilon''(r_s) g(\xi) \left[ 1 + h(r_s) \xi^4 \right] + \varepsilon'_c(r_s) g(\xi) \left[ 1 + h(r_s) \xi^4 \right] \right] + 4 g(\xi) h(r_s) \xi^3 \frac{\partial \xi}{\partial \rho},
\]

(ii) Lee, Yang and Parr Functional (LYP)

A correlation - energy formula due to Colle and Salvetti\(^\text{[86]}\), in which the coorelation energy density is expressed in terms of the electron-density and a Laplacian of the second order Hartree-Fock density matrix, is related as a formula involving the density and local kinetic-energy density by Lee, Yang and Parr\(^\text{[87]}\).

\[
E_c = - a \int \frac{4}{1 + d \rho^{1/3}} \frac{\rho_a \rho_\beta}{\rho} \rho \\
- a b \left[ \omega \left( \rho_a \rho_\beta \left[ 2^{1/3} C_F \left( \rho_a^{\text{HJ3}} + \rho_\beta^{\text{HJ3}} \right) + \left( \frac{47}{18} - \frac{7}{18} \frac{\partial}{\partial} \right) \left| \nabla \rho_a \right|^2 + \left( \frac{5}{2} - \frac{1}{18} \frac{\partial}{\partial} \right) \left| \nabla \rho_\beta \right|^2 \right) \right] \\
\left( \left| \nabla \rho_a \right|^2 + \left| \nabla \rho_\beta \right|^2 \right) \\
- \frac{2}{3} \rho_a^2 \left| \nabla \rho_a \right|^2 + \left( \frac{2}{3} \rho_a^2 - \rho_a' \right) \left| \nabla \rho_a \right|^2 + \left( \frac{2}{3} \rho_\beta^2 - \rho_\beta' \right) \left| \nabla \rho_\beta \right|^2,
\]
where

$$\omega = \frac{\exp(-c\rho^{1/3})}{1 + d\rho^{1/3}} \rho^{-1/3}, \quad \vartheta = c\rho^{1/3} + \frac{d\rho^{1/3}}{1 + d\rho^{1/3}}, \quad C_F = \frac{3}{10} (3\pi^2)^{2/3}$$

The parameters $a$, $b$, $c$ and $d$ were obtained by Colle and Salvetti from a fit to the He atom, $a = 0.04918$, $b = 0.132$, $c = 0.2533$, $d = 0.349$.

Through numerical calculations on a number of atoms, positive ions and molecules of both open and closed-shell type, it is demonstrated that these formulas, like the original Colle - Salvetti formula, give correlation energies within a few percent$^{87,88}$.

(iii) **Perdew and Wang Functional (PW)**

Perdew and Wang$^{89}$ proposed a simple analytic representation of correlation energy $\varepsilon_c$ for a uniform electron gas, as a function of density parameters $r_s$ and relative spin polarization $\xi$. Within the random phase approximation (RPA), this representation allows for the $r_s^{-\frac{3}{2}}$ behaviour as $r_s \to \infty$. Close agreement with numerical RPA values for $\varepsilon_c(r_s, 0)$, $\varepsilon_c(r_s, 1)$ and the spin stiffness $\alpha_c(r_s) = \frac{\delta^2 \varepsilon_c(r_s, \xi = 0)}{\delta \xi^2}$ and recovery of the correct $r_s \ln r_s$ terms for $r_s \to 0$ indicate the appropriateness of the chosen analytic form. Beyond RPA, different parameters for the same analytic form were found by fitting to the Green’s function Monte Carlo data of Ceperley and Alder$^{90}$ taking into account data uncertainties that have been ignored in earlier fits by VWN$^{85}$.

The correlation potential is

$$\varepsilon_c = \int \rho \varepsilon_c(r, \xi) d^3r$$

$$\varepsilon_c(r, \xi) = \xi_c(r, 0) + \alpha_c(r) \frac{f(\xi)}{f''(0)} (1 - \xi^4) + \left[ \varepsilon_c(r, 1) - \varepsilon_c(r, 0) \right] f(\xi) \xi^4$$

$$\text{(58)}$$

$$\text{(59)}$$
where \( f(\xi) = \frac{[(1 + \xi)^{4/3} + (1 - \xi)^{4/3} - 2]}{(2^{4/3} - 2)} \) and \( \xi = 0 \) corresponds to equal \( \alpha \) and \( \beta \) densities, \( \xi = 1 \) corresponds to all \( \alpha \) density and \( \xi = -1 \) corresponds to all \( \beta \) density. Here \( f(0) = 0 \), \( f(\pm) = 1 \), \( f'(0) = 1.709921 \).

The general expression for \( \varepsilon_c \) involves both \( r_s \) and \( \xi \). Its final term performs an interpolation for mixed spin case. The following function \( G \) is used to compute the values of \( \varepsilon_c (r_s, 0) \), \( \varepsilon_c (r_s, 1) \) and \( \alpha_c (r_s) \)

\[
G(r_s, A, \alpha_1, \beta_1, \beta_2, \beta_3, \beta_4, \rho) =
-2A(1 + \alpha_1 r_s) \times \ln\left(1 + \frac{1}{2A(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)}\right)
\]

(60)

In Eq. (60) all the arguments to \( G \) except \( r_s \) are parameters chosen by Perdew and Wang to reproduce accurate calculations on uniform electron gases. The parameter sets differ for \( G \) when it is used to evaluate each of \( \varepsilon_c (r_s, 0) \), \( \varepsilon_c (r_s, 1) \) and \( -\alpha_c (r_s) \).

(c) Hybrid Functionals:

Hartree-Fock theory includes an exchange term as part of its formulation. Recently Becke has formulated function which include a mixture of Hartree-Fock and DFT exchange along with DFT correlation, defining \( E_{xc} \) as

\[
E_{xc}^{\text{hybrid}} = C^{HF} E_x^{HF} + C^{DFT} E_x^{DFT}
\]

(61)

Where \( c \)'s are constant, Becke developed two parameter hybrid functional\(^{(91)}\) and three parameter hybrid functionals\(^{(92)}\). Depending upon combination of functionals various types of hybrid functional available are:
(i) B3PW 91

It is Becke’s three parameter hybrid functional with Perdew/wang\(^{91}\). The exchange - correlation energy \(E_{\text{cx}}\) is given by the formula known as "adiabatic connection" formula\(^{70-73}\). The most convenient one is

\[
E_{\text{cx}} = \int_0^1 U_{xc}^{\lambda} d\lambda
\]

(62)

where \(\lambda\) is an interelectronic coupling strength that "Switches on" the \(1/r_{12}\) coulomb repulsion between electrons, and \(U_{xc}^{\lambda}\) is the potential energy of exchange correlation at intermediate coupling strength \(\lambda\). This formula "connects" the noninteracting Kohn-Sham reference system (\(\lambda = 0\)) to the fully interacting real systems (\(\lambda = 1\)) through a continuum for partially interacting systems \((0 \leq \lambda \leq 1)\), all of which share a common density. \(\lambda = 0\) limit of the coupling strength integration of Eq. (62) is nothing more and nothing less than exact exchange. Therefore exact exchange energy must play a role in highly accurate density functional theories. Accordingly Becke proposed the following exchange -correlation approximation.

\[
E_{\text{xc}}^{\text{B3PW91}} = (1-a_0) E_x^{\text{LDA}} + a_0 E_x^{\text{HF}} + a_s \Delta E_x^{\text{BS}} + E_c^{\text{INDA}} + a_c \Delta E_c^{\text{PW91}}
\]

(63)

Here \(\Delta E_x^{\text{BS}}\) is Becke’s gradient correction (to the LSDA) for exchange functional, and \(\Delta E_c^{\text{PW91}}\) is the Perdew -Wang gradient correction to the correlation functional, \(a_0, a_s\) and \(a_c\) are semi-empirical coefficients to be determined by an appropriate fit to experimental data. The second term replaces some electron-gas exchange with exact exchange to capture the proper small \(\lambda\) limit of Eq. (63). The coefficients \(a_0\) thus reflects the
relative importance of a system’s independent-particle character or equivalently, the rate of onset of correlation as \( \lambda \) increases from zero. The third and fifth terms allow optimum admixtures of exchange and correlation type gradient corrections. The semiempirical coefficients of Eq. (64) have been determined by a linear least squares fit to the 56 atomization energies, 42 ionization potentials, 8 proton affinities and 10 first-row total atomic energies\(^{[93]}\). The resulting optimum values are:

\[
a_0 = 0.20, \ a_\alpha = 0.72, \ a_c = 0.81
\]

**B3LYP**

It is Becke’s three parameter hybrid functional using the LYP correlation functional. B3LYP functional uses the values of \( a_0, a_\alpha, a_c \) as suggested by becke\(^{[92]}\) but uses LYP correlation functional\(^{[87]}\). Since LYP does not have an easily separable local component, the VWN local correlation expression has been used to provide the excess local correlation required.

\[
E_{xc}^{B3LYP} = (1-a_0)E_{xc}^{LSDA} + a_\alpha E_{xc}^{HF} + a_c \Delta E_{xc}^{DSD} + a_c E_{xc}^{LYP} + (1-a_c)E_{xc}^{VWN}
\]

**B3P86**

This is Becke’s three parameter hybrid method with Perdew\(^{[86]}\) functional\(^{[94]}\). The constants \( a_0, a_\alpha, a_c \), have the same value as suggested by Becke\(^{[92]}\).

\[
E_{xc}^{B3P86} = (1-a_0)E_{xc}^{LSDA} + a_\alpha E_{xc}^{HF} + a_c \Delta E_{xc}^{R88} + a_c E_{xc}^{P86}
\]

In our DFT calculation B3LYP functional with 6-31G(d) basis set is used for all calculation reported in this thesis with a view to examine its adequacy in studying potential energy and other molecular properties.
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