CHAPTER 1

General overview and introduction to theoretical methods

1.1 Introduction

The electronic distribution of the molecule is affected by a weak electric perturbation and it can be analyzed with the study of electric response properties. Electric properties such as multipole moments, polarizabilities and hyperpolarizability are studied widely [1-3], due to their applicability in predicting long range atomic and molecular interactions [4]. These fundamental properties play an important role in designing new non-linear optical materials [5]. The higher polarizabilities such as dipole-quadrupole polarizabilities and dipole-octupole polarizabilities have been identified as dominant quantities in spectroscopic measurements such as interaction induced spectroscopy [6, 7] and surface-enhanced Raman scattering[8]. Thus a lot of interest lies in experimental and theoretical studies of electric properties of atoms and molecules. The experimental determinations of these multipole moments and polarizabilities are difficult and hence various theoretical methods have been developed for accurate calculation of these properties [9-16].

Density functional theory (DFT) [17-19] has been used extensively for calculating molecular response properties of a wide variety of atoms, molecules and...
clusters. Many other approaches such as coupled-cluster (CC) and time-dependent self-consistent field (TDSCF) procedure [20, 21], the popular coupled-perturbed Hartree-Fock (CPHF) approach [22], and time-dependent Hartree-Fock (TDHF) based perturbation scheme[23] are available for property calculations. However, among these, DFT has been widely used. While the DFT approach is exact in principle, the popularity of the approach is mainly due to the simple working equations arising from the use of the electron density as the basic variable in the entire framework of the theory. Electron correlation effects and basis sets play important roles in the determination of response properties. DFT is well suited for large molecules and large basis sets and it takes care of electron correlation. However, it scales similarly to the Hartree-Fock theory in terms of computational demand when hybrid functionals are used. DFT calculations without such functionals can, with intelligent use of Fourier transforms or auxiliary basis sets, scale significantly better than Hartree-Fock (HF) method. The true practical applicability of DFT comes from the introduction of a fictitious non-interacting reference system as proposed by Kohn and Sham [24]. This circumvents the explicit construction of the unknown kinetic energy functional and guarantees the accuracy of the approach. Electric properties of molecules are studied to understand their response to an external weak perturbation. Typical examples are molecular dipole polarizabilities and hyperpolarizabilities. Several studies on molecules [25-35] and solids [36] have established that DFT is well suited for these property calculations. More recently, even temperature dependent polarizabilities were studied by first-principle DFT Born-Oppenheimer molecular dynamics (BOMD) simulations [37].

Most of these calculations have been done by using crude energy based numerical finite-field approach. These methods could be highly inaccurate for higher order energy derivatives such as polarizabilities and hyperpolarizabilities. However, the rigorous analytical results are available only for smaller molecules and smaller basis set. Therefore, there is a need to explore computationally feasible methods, which can handle large molecules with reasonable accuracy. The objective of this thesis is to develop a new method which simplifies the rigorous analytical method and gives reasonably accurate results of polarizabilities for large molecules with large basis. In this thesis, we present the non-iterative approach to response properties using DFT \textit{i.e.} the non-iterative approximation to the coupled-perturbed Kohn-Sham (NIA-CPKS) [38-41]. The method has been developed with application
to large molecules in mind. Here we mainly focussed on implementation of NIA-CPKS for dipole-dipole polarizability and dipole-quadrupole polarizability in deMon2k software and its application to the interesting class of systems. To begin with, we introduce here the electric response properties, in Section 1.1. We discuss various *ab initio* methods and evaluation of the response properties with these methods in Section 1.2. In section 1.3 we present the detailed discussion about the density functional theory with special attention to Hohenberg-Kohn (HK) theorem, Kohn-Sham (KS) equation, and the different exchange-correlations functionals. In section 1.4 we discuss the calculation of response properties within DFT using CPKS formalism. We discuss here the non-iterative approach to solve the CPKS equation for calculation of dipole-dipole polarizability. The Section 1.5, focuses mainly on the brief overview of auxiliary density functional theory (ADFT) and the auxiliary density perturbation theory (ADPT) developed within deMon2k. In section 1.6 we briefly review about the molecular dynamics (MD) and properties calculation within molecular dynamic simulation.

### 1.2 Introduction to electric response properties

Depending upon the type of perturbation the molecular properties can be categorised into various types. The perturbation can be due to external electric field, external magnetic field, nuclear magnetic moment or change in the nuclear geometry. In the presence of an arbitrary uniform electric field, the electron distribution of a molecule is distorted, thus it influences the wavefunction and leads to induced dipole moment, quadrupole moment etc. The Hamiltonian of such system depends upon the electric field perturbation. The perturbed Hamiltonian can be expressed as [42],

\[
H(F) = H^0 - \mu_i F_i - \frac{1}{3} \theta_{ij} F_{ij} - \ldots
\]  

(1.1)

\(H^0\) is the unperturbed Hamiltonian, \(\mu_i\) and \(\theta_{ij}\) are the dipole and quadrupole moment operators. \(F_i\) represents an electric field component and \(F_{ij}\) an electric field gradient, which denotes the non-homogeneous nature of the electric field. Energy and multipole moments also show explicit dependence on the electric field. According to Buckingham [43] and McLean and Yoshimine [44] the energy, dipole and
quadrupole moment of a molecule in terms of the static electric field can be written as,

\[ E(F) = E^0 - \mu_0 F_i - \frac{1}{3} \Theta_{ij}^0 F_{ij} - \frac{1}{15} \Omega_{ijk}^0 F_{ijk} - \frac{1}{105} \Phi_{ijkl}^0 F_{ijkl} + \ldots \]

\[ - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{3} A_{ijk} F_{ij} F_k - \frac{1}{6} C_{ijkl} F_{ij} F_k F_l \]

\[ - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{6} B_{ijkl} F_i F_j F_k + \ldots \]  

(1.2)

\[ \mu_i = \mu_0^i + \alpha_{ij} F_j + \frac{1}{3} A_{ijk} F_{jk} + \frac{1}{2} \beta_{ijk} F_{jk} F_k + \frac{1}{3} B_{ijkl} F_{jk} F_k + \ldots \]  

(1.3)

\[ \Theta_{ij} = \Theta_{ij}^0 + A_{k,ij} F_k + C_{ijkl} F_{kl} + \frac{1}{2} B_{ijkl} F_k F_l \]  

(1.4)

Where \( E^0, \mu_0^i, \Theta^0, \Omega^0 \) are the energy and permanent multiple moments of the free molecule, \( \alpha_{ij} \) its dipole-dipole polarizability and \( \beta_{ijk} \) the corresponding (first) hyperpolarizability. \( A_{k,ij} \) is the dipole-quadrupole polarizability and \( B_{ijkl} \) the dipole-dipole-quadrupole hyperpolarizability. The symmetry of the molecule reduces the number of components of above tensor quantities. For example a molecule belonging to \( T_d \) symmetry, there exist only one component of the octupole \( (\Omega_{ijk}) \) and hexadecapole \( (\Phi_{ijkl}) \) moment as well as of the dipole-dipole \( (\alpha_{ij}) \) and dipole-quadrupole \( (A_{k,ij}) \) polarizability. In writing all the above expressions Einstein summation is used, with \( i \) and \( j \) spanning \( x, y \) and \( z \) directions.

It is clear from the energy expression that the dipole moment and polarizability of molecule are the first and second derivatives of ground state energy with respect to electric field perturbation at zero fields respectively. Similarly, dipole-quadrupole polarizability is the second derivative of energy with respect to electric field perturbation, \( F \) and field gradient, \( F' \) at their zero values.

\[ \mu_i = - \left( \frac{\partial E}{\partial F_i} \right)_{F=0} \]  

(1.5)

\[ \alpha_{ij} = - \left( \frac{\partial^2 E}{\partial F_i \partial F_j} \right)_{F=0} \]  

(1.6)

\[ A_{i,jk} = - \left( \frac{\partial^2 E}{\partial F_i \partial F_{jk}} \right)_{F=0,F'=0} \]  

(1.7)

The external electric field may either be time independent, which lead to static properties, or time dependent, leading to dynamic properties. Time-dependent fields are usually associated with electromagnetic radiation characterized by a frequency,
and static properties may be considered as the limiting case of dynamic properties when the frequency goes to zero.

According to Helmann-Feynman theorem [45,46], for the exact wavefunction and variational method the first derivative of energy with respect to electric field is equal to the expectation value of the derivative of the Hamiltonian. For electric properties, the first derivative of energy is equal to the expectation value of dipole moment operator. Further for a variational method, according to Wigner’s (2n+1) rule [47], response up 3rd order can be calculated from the 1st order response of wave function or density.

1.3 Wavefunction based quantum chemical methods

The main objective of most quantum chemical approaches is to solve the time-independent, non-relativistic Schrödinger equation [48, 49]

\[ \hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, \ldots \vec{x}_N, \vec{R}_1, \vec{R}_2, \ldots \vec{R}_M) = E_i\Psi_i(\vec{x}_1, \vec{x}_2, \ldots \vec{x}_N, \vec{R}_1, \vec{R}_2, \ldots \vec{R}_M) \]  

(1.8)

where \( \hat{H} \) is the Hamiltonian operator for the total energy of the molecular system consisting of \( M \) nuclei and \( N \) electrons in the absence of magnetic or electric fields. It is composed of kinetic energy of constituent particles, potential energy due to attractive and repulsive interaction amongst the particles.

\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{M} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} \]

(1.9)

In the above equation, \( R_A \) and \( r_i \) are spatial coordinates of \( A^{th} \) nucleus and \( i^{th} \) electron respectively. \( M_A \) is the ratio of the mass of nucleus \( A \) to the mass of an electron, and \( Z_A \) is the atomic number of nucleus \( A \). The Laplacian operators \( \nabla_i^2 \) and \( \nabla_A^2 \) involve differentiation with respect to the coordinates of the \( i^{th} \) electron and the \( A^{th} \) nucleus. The first term in Eq. (1.9) is the operator for the kinetic energy of the electrons; the second term is the operator for the kinetic energy of the nuclei; the third term
represents the coulomb attraction between electrons and nuclei; the fourth and fifth terms represent the repulsion between electrons and between nuclei, respectively. $\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_M)$ stands for the wave function of the $i^{th}$ state of the system, which depends on the 3N spatial coordinates $\{\vec{r}_i\}$, and the N spin coordinates $\{\vec{s}_i\}$ of the electrons, which are collectively termed $\{\vec{x}_i\}$ and the 3M spatial coordinates of the nuclei, $\{\vec{R}_i\}$ . The wave function contains all the information that can be possibly known about the system it describes. Ultimately, $E_i$ is the numerical value of the energy of the state described by $\Psi_i$.

Solution of the eigenvalue problem Eq. (1.8) yields stationary state energies and the corresponding eigenfunctions. In absence of external perturbation, atoms and molecules are assumed to be in one of these states. It is however, very difficult to solve Eq. (1.8), even for small systems. Since, nuclei are much heavier than electrons, while considering electronic motions, they can virtually be assumed to be stationary. This is known as frozen-nuclei Born-Oppenheimer approximation (BOA) [50]. As a result of this approximation, the 1st term in Eq. (1.9), the kinetic energy of nuclei drops out and the inter-nuclear repulsion energy (third term in Eq. (1.9)) becomes constant. The constant added to an operator does not affect the eigenfunctions and simply adds to the eigenvalues. Thus the complete Hamiltonian given in equation (1.9) reduces to the so-called electronic Hamiltonian

$$\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|r_i - R_A|} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{1}{|R_A - R_B|}$$

$$= \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}$$  \hspace{1cm} (1.10)

The eigenvalues of the electronic Hamiltonian are the total electronic energies of the corresponding stationary states. The corresponding eigenfunctions are parametrically dependent on nuclear coordinates. The total energy $E_{\text{tot}}$ is then the sum of $E_{\text{elec}}$ and the constant nuclear repulsion term,

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{nuc}}$$  \hspace{1cm} (1.11)

$$E_{\text{nuc}} = \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{1}{|R_A - R_B|}$$  \hspace{1cm} (1.12)
Addition of the inter-nuclear repulsion energy to the total electronic energy provides and effective potential energy surface (PES) $V_{\text{eff}}(R_1, R_2, \ldots R_M)$ of nuclear motion. The PES resulting from different electronic states is generally well separated and the interaction between two PES is negligible. Due to this, the nuclear motion is well separated from the electronic motion. Thus BOA turns to a very good approximation for electronic structure calculations as the problem of $M + N$ entities reduces to $N$-electron problem with fixed nuclei. The concept of PES serves to bring back chemist's view of molecules, equilibrium structure, etc. in terms of energy.

However, even with BO approximation, it is difficult to solve a many electron problem. Except for few problems the Schrödinger equation cannot be solved exactly, so methods of approximation are needed in order to tackle these problems. The two basic methods of approximation are variation [51] and perturbation [48, 52, 53] theories. In variation theory, an initial guess is made as to the shape of the wavefunction, which is then optimized to approximate the true wavefunction for the problem. Thus variational principle gives the recipe for systematically approaching the wave function of the ground state $\Psi_0$, i.e., the state of lowest energy $E_0$. According to variational principle the energy computed as the expectation value of the Hamilton operator $\hat{H}$ from any well behaved, guessed $\Psi_{\text{trial}}$ will be an upper bound to the true energy of the ground state.

$$\frac{\langle \Psi_{\text{trial}} | H | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle} = E[\Psi_{\text{trial}}] \geq E_0 \quad \text{(1.13)}$$

The solution to Hartree-Fock and CI method is obtained variationally. In perturbation theory, the total Hamiltonian of the system is divided into two parts, a zeroth-order part, $H_0$ which has known eigenfunctions and eigenvalues, and a perturbation, $V$. The wavefunctions from the part of the Schrödinger equation in which the solution is known are used as a starting point and then modified to approximate the true wavefunction for the Schrödinger equation of interest. Perturbation methods can be used in quantum mechanics for adding corrections to solutions that employ an independent-particle approximation, and the theoretical framework is then called many-body perturbation theory (MBPT). The traditional coupled cluster method [54-58], is neither variational nor perturbative. This method has been established as the
Chapter 1 Introduction

1.4 Hatree-Fock theory

HF is the central starting point for most ab initio quantum chemistry methods. The method assumes that the exact, \(N\)-body wave function of the system can be approximated by a single Slater determinant, an antisymmetrized product of one-electron wave functions (i.e., orbitals)[48,59,60].

\[
\Phi_0(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N) = |\chi_i(x_1)\chi_j(x_2) \ldots \chi_k(x_N)\rangle
\]  

(1.14)

By invoking the variational method, one can derive a set of \(N\)-coupled equations for the \(N\) spin orbitals. The method of Lagrange undetermined multipliers is used to minimize the energy with respect to the spin orbitals [48]. In the process, the spin-orbitals are varied under the constraint that the spin-orbitals form an orthonormal set. The variational minimization of energy with respect to choice of spin orbitals leads to Hartree-Fock equation. The Hartree-Fock equation is the eigen value equation

\[
\hat{f}(\vec{x})\chi_a(\vec{x}) = \varepsilon_a\chi_a(\vec{x})
\]  

(1.15)

Where

\[
\hat{f}(\vec{x}) = \hat{T}_e + \hat{V}_{ne} + \nu_{HF}(\vec{x})
\]  

(1.16)

\(\hat{f}(\vec{x})\) is Fock operator, an effective one-electron Hamiltonian operator. It is sum of the kinetic energy operator \(\hat{T}_e\), \(\hat{V}_{ne}\), the nuclearelectronic interaction operator and \(\nu_{HF}(\vec{x})\), the average potential experienced by an electrons due to motions of all other electrons.

\[
\nu_{HF}(\vec{x}) = \sum_{j=1}^{N} J_j(\vec{x}) - \sum_{j=1}^{N} K_j(\vec{x})
\]  

(1.17)

It includes the average Coulomb interaction defined by local operator \(J_j(\vec{x})\) and a non-classical potential represented by a non-local operator \(K_j(\vec{x})\) known as exchange potential. The exchange potential is consequence of the anti-symmetric nature of the wavefunction. The Fock operator being dependant on its eigenfunctions, the set of equations (1.15) - (1.17) are solved iteratively until some self consistency is achieved between successive equations. As a result a Slater
determinant corresponding to the best set of spin-orbitals and consequently the minimum energy or the ground state energy of the system is obtained.

For atoms, the HF equations can be exactly solved as integro-differential equations. For molecules, however, the explicit integration of the two-electron interaction terms is difficult as the orbitals involved are centred at different nuclei. Hence Roothan [61] introduced a finite set of Gaussian functions to define the spatial parts of atomic orbitals, which are then transformed to molecular orbital basis to achieve orthonormalization. For closed-shell systems, the spin-orbitals with opposite (spin-up and spin-down) spin functions are paired up and the problem can be simplified by using only spatial orbitals after spin-integration. This leads to Roothan-Hall equations and the method is known as restricted HF (RHF). The open-shell systems also have most of the electrons paired up and can be solved by restricted open-shell HF (ROHF) method. On the other hand, this simplification of electron pairing may not be considered and one may explicitly solve the HF equations using spin-orbitals. The method is called unrestricted HF (UHF) and leads to Pople-Nesbet equations. While an RHF or ROHF determinant is a pure eigenfunction of total spin operator, UHF determinant, in general, is not.

1.5 Electron correlation and post HF methods

The major simplification to the HF theory comes from independent particle picture by approximating wavefunction as a single Slater determinant. HF theory only accounts for the average electron–electron interactions, and consequently neglects the correlation between electrons. Physically it corresponds to the motion of the electrons being correlated. The difference between exact energy and HF energy is called correlation energy as it arises due to partial ignorance of the electron-electron interactions. Though HF determinant recovers almost 99% of the total energy the remaining correlation energy is usually very important for describing chemical phenomena. Within the HF approximation the correlation between electrons with parallel spin is accounted by the electron exchange term. This type of correlation is called as Fermi correlation, which prevents two electrons of parallel spin being found at the same point in space. However, Coulomb correlation, the correlation between the electrons of opposite spin is neglected by the single determinant picture. The electron correlation can also be categorised as static and
dynamic correlation. The dynamic contribution is associated with the “instant” correlation between electrons, such as between those occupying the same spatial orbital. It is the correlation of the movement of electron. The static correlation is associated with electrons avoiding each other on a more “permanent” basis, such as those occupying different spatial orbitals. This is also called a near-degeneracy effect, as it becomes important for systems where different orbitals (configurations) have similar energies. Methods that include electron correlation require a multi-determinant wave function. Since HF is the best single determinant wave function for the ground state, it is generally used as starting guess for correlated methods. Multi-determinant methods are computationally much more involved than the HF model, but can generate results that systematically approach the exact solution of the Schrödinger equation. The correlation energy can be recovered by improving the approximations made in HF theory. This leads to various post HF theories which are collectively termed as many-body methods.

1.5.1 Configuration interaction

Configuration interaction (CI) wavefunction is expressed as a linear combination of ground and excited determinants. HF determinant is the ground state determinant and other determinants are defined as excitations with respect to HF occupancies [48, 62, 63]. Thus the configurations can be singly excited, doubly excited and so on, up to N-tuply excited with respect to HF configuration. The total wavefunction can thus be represented as

$$\Psi = \Phi_0 + \sum_{i\in occ} \sum_{a\in virt} C_i^a \Phi_i^a + \sum_{i,j\in occ} \sum_{a,b\in virt} C_{ij}^{ab} \Phi_{ij}^{ab} + \ldots$$

(1.18)

Intermediate normalization has been used in the above expansion. The $\Phi_i^a$ indicates a singly excited determinant formed by excitation of electron from $i-th$ orbital (occupied) in HF determinant to the $a-th$ (virtual) orbital. Similarly, $\Phi_{ij}^{ab}$ indicates doubly excited determinant obtained by exciting the electrons from $i-th$ and $j-th$ orbitals to $a-th$ and $b-th$ orbitals respectively. When all possible excitations are considered in expansion the method is called as full CI. The corresponding coefficients are obtained using linear variation method. This leads to
The eigenvalue problem for the Hamiltonian matrix. The matrix elements are calculated using Slater-Condon rules [48]. The lowest eigenvalue and the eigenvectors correspond to the ground state of the system and rest of them correspond to excited states of the system. The dimensions of the wavefunctions increase rapidly with the number of electrons as well as basis functions and practically, it becomes impossible to use FCI even for small molecules with moderate size basis sets. Thus truncation of the CI expansion solves the problem and one can get well-correlated wavefunctions and well-correlated energies as per the level of truncation. The expansion of the wavefunction formed by excluding all the configurations except HF and doubly excited configurations is known as CI doubles (CID). Truncation of CI expansion to doubles recovers most of the correlation energy. The molecular properties like dipole moments, polarizabilities, etc. are defined by one-electron operator. Hence the singly excited determinants can be included along with the doubly excited ones. The method is called CI singles and doubles (CISD) and describes the one-electron properties more accurately. Although singly excited determinants do not directly mix with HF, they interact through the doubly excited determinants and further improve the correlation energy. Accuracy can be improved by including the higher excited configurations leading to CISD and triples (CISDT), CISDT and quadruples (CISDTQ) and so on.

The truncation of CI expansion destroys the size-consistency and size-extensivity of the wavefunction. Size-consistency refers to additive separability of the energy during fragmentation, that is, if a molecule AB dissociates into its fragments A and B then energy of the system should follow the following relation

$$E_{AB} = E_A + E_B$$

(1.19)

Size-extensivity is related to scaling of the energy of the system with number of electrons. Due to non-interacting picture, HF energy properly scales with the number of electrons. Hence, size-extensivity is considered as a requirement of correlated methods. If total energy (and hence, the correlation energy) of a system approximately varies linearly with the number of electrons, the method is said to be size-extensive. The truncated CI has found to show the sub-linear dependence [48] of energy with the number of electrons, thus misinterpreting zero correlation energy per electron as the number of electrons tends to infinity.
1.5.2 Many body perturbation theory

The basic idea behind the perturbation theory is that the problem in hand is just slightly different than the problem that has been already solved either exactly or approximately [64-66]. In mathematical language this can be expressed by partitioning the Hamiltonian into two parts. First term is the reference term \( H_0 \) and second is the perturbation term, \( V \), which is small compared to \( H_0 \). Thus the total Hamiltonian is written as

\[
\hat{H} = \hat{H}_0 + \lambda V'
\]  

(1.20)

The reference term \( H_0 \) is the dominant part of the total Hamiltonian and its solution is known. \( H_0 \) is termed as zero\(^{th}\) order Hamiltonian. The eigenfunctions \( \{ \Psi_i^0 \} \) of \( H_0 \) form a complete set with the corresponding eigenvalues denoted by \( E_i^0 \). The second term, \( V \), of equation 1.20 is unknown and it is viewed as a perturbation to the zero\(^{th}\) order Hamiltonian. Perturbation method gives the systematic procedure for adding correction to solution that has been obtained from independent particle approximation. \( \lambda \) is the perturbation parameter which determine the strength of the perturbation. As the perturbation is increased from zero to a finite value, the energy and wave function must also change continuously, and they can be written as a Taylor expansion in powers of the perturbation parameter \( \lambda \).

\[
\Psi_i = \Psi_i^0 + \lambda \Psi_i^1 + \frac{\lambda^2}{2!} \Psi_i^2 + \frac{\lambda^3}{3!} \Psi_i^3 + \ldots
\]

\[
E_i = E_i^0 + \lambda E_i^1 + \frac{\lambda^2}{2!} E_i^2 + \frac{\lambda^3}{3!} E_i^3 + \ldots
\]  

(1.21)

When \( \lambda = 0 \), \( H = H_0 \) and \( E_i = E_i^0 \) This is unperturbed or is zeroth order wavefunction and energy. at \( \lambda = 1 \) system is completely perturbed corresponding to the stationary states of the exact Hamiltonian. The \( \Psi_i^1, \Psi_i^2 \ldots \) and \( E_i^1, E_i^2 \ldots \) are the first-order, second-order, etc., corrections. The parameter \( \lambda \) will eventually be set equal to 1, and the n\(^{th}\)-order energy or wave function becomes a sum of all terms up to order n.

The MBPT is divided into various methods depending upon the way wavefunction at various orders is solved. The one developed by Brillouin and Wigner known as Brillouin-Wigner perturbation theory (BWPT) [66] and the other one developed by Rayleigh and Schrödinger known as Rayleigh-Schrödinger perturbation theory (RSPT) [64, 66, 67]. Both these approaches use Taylor series
expansion around the solutions of the zeroth order part. Also depending upon the partitioning of Hamiltonian there are two variants, namely Møller-Plesset (MP) and Epstein-Nesbet (EN) perturbation theories. In RSPT, the quantities in Eq. (1.21) are substituted in the Schrödinger equation. The terms with fixed power of \( V \) are then collected together and solved for energies and wavefunctions at various orders. In MP theory the zeroth-order wave function is an exact eigenfunction of the Fock operator, which thus serves as the unperturbed operator. The perturbation is the correlation potential. Thus MP-theory is a special application of RSPT. The MP based RSPT is now commonly used for correlated calculations of atoms and molecules. RSPT with MP partitioning leads to a size-extensive perturbation series. The acronyms MP2, MP4, MBPT(n), etc. have become very popular because of accuracy and relative simplicity of the method.

1.5.3 Coupled-cluster theory

The CC method is the most accurate quantum chemical method which can be applied for small to medium sized molecule [68-72]. The coupled-cluster (CC) methods include all corrections of a given type to infinite order. The ground state wavefunction of an N-electron system is obtained by action of an exponential wave-operator on a reference wavefunction, usually, the Hartree-Fock configuration.

\[
|\Psi_0\rangle = e^T |\Phi_0\rangle \tag{1.22}
\]

\( T \) is cluster operator and it is defined as the sum of one-electron excitation operator, two-electron excitation operator and so on up to N-electron excitation operators.

\[
T = T_1 + T_2 + T_3 + \cdots T_{N_{elec}} \tag{1.23}
\]

The \( T_i \) operator acting on an HF reference wave function \( \Phi_0 \) generates all \( i^{th} \) excited Slater determinants.

\[
T_1 \Phi_0 = \sum_{l} \sum_{a} t_l^a \Phi_l^a
\]

\[
T_2 \Phi_0 = \sum_{l<j} \sum_{a<b} t_{ij}^{ab} \Phi_{ij}^{ab} \tag{1.24}
\]
the expansion coefficients $t$ is termed as amplitude corresponding to the cluster operators $T$. With the CC wave function in eq. (1.22) the Schrödinger equation becomes,

$$\hat{H} e^T |\Phi_0\rangle = E e^T |\Phi_0\rangle$$  \hspace{1cm} (1.25)

Above equation can be solved by variational [73-75] or non-variational approach. The standard formulation of coupled cluster theory is nonvariational. In traditional formulation of CC method the equations for energy and cluster amplitudes can be obtained by method of projection wherein the Schrödinger equation (1.25) is projected from left by HF configuration and excited configurations. The same set of equations can also be obtained by similarity transformation method.

If all cluster operators up to $T_N$ are included in $T$; the method is known as full CC (FCC) and the CC wave function is equivalent to FCI. The exponential nature of the FCC wave operator makes it difficult to practice it even for the small molecules. The cluster operator must therefore be truncated at some excitation level. The lowest level of approximation is therefore, $T = T_2$, referred to as CCD. Using $T = T_1 + T_2$ gives the CCSD model, which is only slightly more demanding than CCD, and yields a more complete model. Both CCD and CCSD involve a computational effort that scales $M_{\text{basis}}^6$ in the limit of a large basis set. The next higher level is CCSDT model. This scales to the order $M_{\text{basis}}^8$. CCSD is the most commonly used CC anasatz. Unlike CISD, CCSD (or in general, any truncated CC) continues to be size-consistent and size-extensive. This is because of the exponential nature of the wave operator, which includes higher excitations through the products of $T_1$ and $T_2$. Non-linearity of CC equation and non-variational nature are the only limitations of the method. Despite of truncation it gives highly accurate and systematically improving results during every iterative step. Provided the reference fragments correctly, the exponential nature of the wave operator guarantees the size-consistency of the overall wave function and energy. Thus CC is the most reliable method for calculation various chemical properties of molecule [76-78]. Ample of research have been done for further improvement of CC method and its development for calculation of various properties [79-83].
1.6 Density functional theory

A wavefunction for N electrons depends upon the 3N spatial coordinates of electrons and N spin coordinates. However, density $\rho(r)$ depends only upon 3 coordinates $(x, y, z)$ and the spin. The basic idea of the density functional theory is to replace the complicated wavefunction by simpler density $\rho(r)$. The Thomas-Fermi (TF) model was in many aspects very successful and showed the basic steps to obtain the density functional for the total energy [84, 85]. In TF model the electrons are treated as independent particles forming a uniform electron gas and the electron-electron repulsion energy arises solely due to electrostatic interactions. In literature model has been used for calculations on atoms and molecules [86-88]. However, the accuracy of the model is limited. The TF method was found to give a very crude description of the electron density and the electrostatic potential. It was shown that the TF scheme is exact in the limit of infinite nuclear charge. The model has shown the infinite charge density at the nucleus. Also, the charge density does not decay exponentially away from the nucleus of the atom. The method does not account for binding of atoms to give molecules or solids. The model lacks the shell structure in the atom. All these and a few other defects have led to the modification of the model. Subsequently some modifications were applied to the TF model by Dirac, wherein, an exchange term was added to the TF equations [89]. This model was called the Thomas-Fermi-Dirac (TFD) model. Von Weizsacker added a gradient term to the kinetic energy term of the TF model. This model came to be known as Thomas-Fermi-Weizsacker (TFW) model [90]. Despite the flaws in the TF model, it came to be known as the first approximation to the exact description of the ground state of any system in terms of the density; this turns out to be a density functional description, where, all properties of a system can be expressed in terms of the electron density.

The modern formulation of density functional theory originated with the fundamental theorems of Hohenberg and Kohn [91].

**First Hohenberg-Kohn Theorem:** The external potential $\nu(r)$ is determined, within a trivial additive constant, by the electron density, $\rho(r)$.

In simple words, the electronic density provides the information of the number of electrons, by integration, and the position and type of nuclei, by cusps in the density.
distribution. The Hamilton operator, can be built with this information and thus the energy can be obtained by solving the Schrödinger equation. Since the wave function depends on the nature of the Hamiltonian and this operator is determined by the electronic density. Thus all (ground state) properties of the system are determined by the electronic density. The ground state energy of the system is written as a functional of density $\rho(r)$.

$$ E[\rho] = F_{HK}[\rho] + \int \rho(r) v(r) dr $$  \hspace{1cm} (1.26)

$F_{HK}[\rho]$ is the HK universal functional of density $\rho(r)$ and it can be split into two contributions, the kinetic energy functional $T[\rho]$ and a functional that contains all remaining electron-electron interactions $V_{ee}$

$$ F[\rho] = T[\rho] + V_{ee}[\rho] $$  \hspace{1cm} (1.27)

$V_{ee}[\rho]$ contains the classical Coulomb interaction and the electronic quantum interaction, known as exchange-correlation energy. Thus the exact ground state energy of the system can be determined once the form of the $F_{HK}[\rho]$ is known. However, the exact form of the universal HK functional is unknown. Hence first HK theorem is thus only an existence theorem for the energy functional.

The second HK theorem provides the procedure to obtain the energy functional. It gives an energy variational principle to the energy functional.

**Second HK theorem:** For a trial density $\rho_t(r)$, such that

$$ \int \rho_t(r) dr = N \quad \text{and} \quad \rho_t(r) \geq 0 $$

$$ E_0 \leq E[\rho_t(r)] $$  \hspace{1cm} (1.28)

Which says that the energy functional is always greater than or equal to the exact ground state energy, $E_0$. As stated above the determination of the form of the $F_{HK}[\rho]$ is the crucial part in construction of the energy functional for obtaining the exact ground state energy.

### 1.6.1 Kohn-Sham method

In 1965, Kohn and Sham [92] made a major step towards quantitative modelling of electronic structure, by introducing an elegant way for the evaluation of kinetic energy functional. They proposed the introduction of orbitals from a non-interacting reference system. For a non-interacting system the wave-function is just
the antisymmetric product of single particle solutions (known as orbitals), $\psi_i$. The exact expression for the kinetic energy of the non-interacting Kohn-Sham (KS) system is given as,

$$T_{KS}[\rho] = -\frac{1}{2} \sum_i^{occ} \langle \psi_i | \nabla^2 | \psi_i \rangle$$  \hspace{1cm} (1.29)

Occupied orbitals are labelled with $i$ or $j$, and virtual orbitals are labelled with $a$ or $b$. Letters $p$ or $q$ will be used to label any molecular orbital, independent of its occupation. The electronic density which connects the fictitious non-interacting system with the real system is given by:

$$\rho(r) = \sum_i^{occ} |\psi_i(r)|^2$$ \hspace{1cm} (1.30)

In most approaches, $T_{KS}[\rho]$ is used as a first approximation to the kinetic energy of the real system. Using the explicit expression for the Coulomb interaction the energy functional is given by:

$$E[\rho] = T_{KS}[\rho] + \int v(r) \rho(r) dr + \frac{1}{2} \int \int \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + E_{xc}[\rho]$$ \hspace{1cm} (1.31)

$E_{xc}[\rho]$ is the KS exchange-correlation energy functional. The orbitals for the noninteracting reference system are obtained by minimizing (1.31) imposing the restriction of orthonormality

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$ \hspace{1cm} (1.32)

The results obtained from the variation of (1.31) subject to orthonormality of orbitals are the single-particle Kohn-Sham equations. Their canonical form is given by:

$$\left( -\frac{1}{2} \nabla^2 + v(r) + \int \frac{\rho(r')}{|r - r'|} dr' + u_{xc}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r) \forall i$$ \hspace{1cm} (1.33)

Here $u_{xc}[\rho]$ is the exchange-correlation potential. This is obtained as the functional derivative of the exchange-correlation energy:

$$u_{xc}(r) \equiv \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$ \hspace{1cm} (1.34)

KS method eliminates the unknown kinetic energy functional by introducing orbitals of a fictitious non-interacting reference system. However, the exchange-correlation
energy functional is still unknown. Various approximations are made to define the form of \( E_{xc}[\rho] \). The quality of any DFT calculation using the KS method is determined mainly by the approximation used for the evaluation of \( E_{xc}[\rho] \). The most common approximation is the local density approximation (LDA) in which the Dirac exchange \([93]\) is combined with some approximation for the ideal electron gas correlation, like the one proposed by Vosko, Wilk and Nusair (VWN) \([94]\). More sophisticated approaches include the generalized gradient approximations (GGA) \([95, 96]\) like BLYP \([97-100]\) and PBE \([101]\) or the hybrid functionals \([102]\) like B3LYP. As the name suggests the \( E_{xc}[\rho] \) is evaluated by an integral over a function that depends only on the density and its gradient at a given point in space.

Compared to the orbital-free DFT approaches the kinetic energy functional is evaluated more accurately in Kohn-Sham DFT. The other advantage for Kohn-Sham approach is that the technical knowledge can be inherited from \textit{ab initio} methods. Kohn-Sham method is a very close analogue to the Hartree-Fock method and many ideas can be exported from each other. Programs like ADF \([103, 104]\) or DMol \([105]\) use numerical basis sets for the expansion of the Kohn-Sham orbitals. However, deMon2k programme \([106]\), use the linear combination of Gaussian type orbitals (LCGTO) approximation with analytic Gaussian functions. In both cases the equations are recast in matrix form yielding Roothaan-Hall type equation systems \([61a, 107]\).

The ordinary DFT is developed for calculation of ground stationary states, thus one cannot use it for calculation of optical properties or to treat excited states. Time dependent DFT has been developed for treatment of excited states within DFT framework. Time dependent density functional theory (TDDFT) is based on Runge-Gross theorem \([108-114]\) which is the time dependent analogue of the first Hohenberg-Kohn theorem. The required variational principle is the Frenkel principle \([115,116]\). In addition, in time dependent Kohn-Sham theory it is assumed that a time dependent non-interacting reference system exists, which has density propagation equal to the real density \( \rho(r, t) \)[117].

### 1.6.2 Auxiliary density functional theory

In the LCGTO-DFT approach, the Kohn-Sham molecular orbitals are expanded into atomic orbitals. Here the molecular integrals are evaluated using
contracted (Cartesian) Gaussian type orbital (CGTO) functions. Using linear combination of GTOs the (KS-SCF) energy expression for close shell system is given as,

\[ E_{SCF} = \sum_{\mu, \nu} P_{\mu \nu} H_{\mu \nu} + \frac{1}{2} \sum_{\mu, \nu} \sum_{\sigma, \tau} P_{\mu \nu} P_{\sigma \tau} \langle \mu \nu \| \sigma \tau \rangle + E_{xc}[\rho] \]  

(1.35)

where \( \mu \) and \( \nu \) are the basis function and \( P_{\mu \nu} \) is an element of the density matrix. \( H_{\mu \nu} \) is matrix element of the core Hamiltonian. The core Hamiltonian contains kinetic energy and nuclear attraction integrals as well as one electron perturbation terms. The second term in eq. (1.35) represents the classical Coulomb repulsion between the electrons and involves four-centre electron-electron repulsion integrals. Here the two-electron Coulomb operator is denoted by the \( \| \) symbol. The last term represents the exchange-correlation energy. In deMon2k [106] auxiliary functions are used to fit the charge density. The approximate density \( \tilde{\rho}(r) \) is expanded into primitive Hermite Gaussians \( \tilde{k}(r) \) centred on atoms [118,119] as,

\[ \tilde{\rho}(r) = \sum_{k} x_{k} \tilde{k}(r) \]  

(1.36)

Here the primitive Hermite Gaussian auxiliary functions are denoted by a bar. The above auxiliary density is used for the variational fitting of the Coulomb potential [120,121]. As a result, the \( N^4 \) scaling of Coulomb integrals is avoided. In ADFT the approximated density is also used for the calculation of the exchange-correlation energy [122]. The ADFT energy expression is given as,

\[ E_{SCF} = \sum_{\mu, \nu} P_{\mu \nu} H_{\mu \nu} + \sum_{\mu, \nu} \sum_{k} P_{\mu \nu} \langle \mu \nu \| \tilde{k} \rangle x_{k} - \frac{1}{2} \sum_{k, l} x_{k} x_{l} \langle \tilde{k} \| \tilde{l} \rangle + E_{xc} \]  

(1.37)

The fitting coefficients \( x_{k} \) are obtained by the variational minimization of the difference between the Kohn-Sham and auxiliary density in a Coulombic metric according to Dunlap [108]. Different to the original work from Dunlap et al. no charge conservation constraint is employed [123]. As a result the following inhomogeneous equation system [124] for the determination of the fitting coefficients collected in the vector \( x \) is obtained:

\[ G \cdot x = J \]  

(1.38)
Here $G$ and $J$ denote the Coulomb matrix and vector. They are defined as:

$$G_{k\ell} = \langle k\|\ell \rangle$$  \hspace{1cm} (1.39)

$$J_k = \sum_{\mu,\nu} P_{\mu\nu} \langle \mu\nu\|k \rangle$$  \hspace{1cm} (1.40)

The formal solution to this equation is given by$^{69}$,

$$x_k = \sum_l G_{k\ell}^{-1} J_l = \sum_l \sum_{\mu,\nu} \langle k\|l \rangle^{-1} \langle l\|\mu\nu \rangle P_{\mu\nu}$$  \hspace{1cm} (1.41)

For the calculation of the exchange-correlation contribution in ADFT it is convenient to introduce a second set of fitting coefficients. These so-called exchange-correlation fitting coefficients are given by$^{125}$:

$$z_k \equiv \sum_l \langle k\|l \rangle^{-1} \langle l\|\rho_{xc}[\bar{\rho}] \rangle$$  \hspace{1cm} (1.42)

It should be noted that the calculation of the exchange-correlation fitting coefficients involves a numerical integration and that these coefficients are usually spin polarized. The ADFT Kohn-Sham matrix elements are then given as,

$$K_{\mu\nu} = H_{\mu\nu} + \sum_k \langle \mu\nu\|k \rangle (x_k + z_k)$$  \hspace{1cm} (1.43)

As can be seen from the above equation the ADFT Kohn-Sham matrix elements depend only on the Coulomb and exchange-correlation coefficients. Thus only the approximated density is numerically calculated on a grid. Because this density is linearly scaled by construction, the necessary grid work is considerably reduced. In fact, calculation of the Kohn-Sham potential is in ADFT identical to orbital free DFT approaches with the auxiliary density as basic variable. This has also significant importance for the calculation of higher energy derivatives which we will see in the next section.

1.7 Electric response properties: methods of calculation

In section 1.1 we discussed the electric response properties using derivative formula. These properties can be calculated either numerically or analytically. A
straight forward method is to solve Schrödinger equation for the system of interest at various field values and obtain the numerical derivatives of energy by finite difference method. This approach is known as finite-field approach and requires very accurate evaluation of wavefunction and energy, although, no computational developments are required. But the method involves numerical instabilities. In analytical method, explicit expressions for wavefunction derivatives are solved and used to obtain molecular properties. There are three main methods available for calculation of response properties, namely, derivative techniques, perturbation theory based on the energy and perturbation theory based on expectation values of properties, often called response or propagator methods. For variationally optimized wave functions (HF or multi configuration SCF) the $2n + 1$ rule is applied which says that the knowledge of the $n^{th}$ derivative or response of the wave function is sufficient for calculating a property to order $2n + 1[47]$. For non-variational wave functions the $n^{th}$-order wave function response is required for calculating the $n^{th}$-order property. However, this can be avoided by a technique first illustrated by Handy and Schaefer for CISD geometry derivatives, often referred to as the Z-vector method [126]. This method has been later generalized for other types of wave functions and derivatives by formulating it in terms of a Lagrange function [127]. As per Hallman-Feyman theorem, though the calculation of first order response is avoided for variationally optimized wavefunction, it is necessary for second (and higher) derivatives. Therefore, for calculation of polarizabilities (second order property) we need wavefunction response of first order. Generally the CPHF method is used to compute analytical gradients from single-determinant (HF) reference for calculation of polarizabilities and hyperpolarizabilities. The CPHF equations need to be solved iteratively due to implicit dependence of coupled equations on first order response. The propagator or response method known as random phase approximation (RPA) [128] is identical to CPHF or TDHF [129,130] for static case in given basis. When the coupled perturbed approach is implemented in DFT it is known as coupled perturbed Kohn-Sham method (CPKS). Recently, two non iterative methods have been presented for calculation of first order response of density. The first method we discuss here is known as non-iterative approximation to coupled perturbed Kohn-Sham (NIA-CPKS) method [38, 39, 131-133]. NIA-CPKS is the simplification to the iterative CPKS formalism. This is numerical-analytical
method. There is another non-iterative method proposed by Roberto et al. [124, 134] is an alternative to the CPKS approach for calculation of electric response properties. This method is known as auxiliary density perturbation theory (ADPT).

1.7.1 Non-iterative approximation to coupled perturbed Kohn-Sham (NIA-CPKS)

CPKS is the conventional approach used for calculation of static response of the electric field perturbation [135-142]. The derivative of KS equation with respect to field gives the CPKS equation.

\[
\mathbf{K}^{(\lambda)} \mathbf{c} + \mathbf{K} \mathbf{c}^{(\lambda)} = \mathbf{S}^{(\lambda)} \mathbf{c} \varepsilon + \mathbf{S} \mathbf{c}^{(\lambda)} \varepsilon + \mathbf{S} \mathbf{c} \varepsilon^{(\lambda)}
\]  

(1.44)

In case of electric perturbation, the derivative of KS-operator matrix, \(\mathbf{K}^{(\lambda)}\), consists of the two-electron and the response term. The \(\mathbf{K}^{(\lambda)}\) has an explicit dependence on perturbed coefficients \(\mathbf{c}^{(\lambda)}\) and as a result the CPKS equation need to be solved iteratively for self consistency. The two electron term in \(\mathbf{K}^{(\lambda)}\) constitutes complicated functional derivative of Coulomb as well as the exchange-correlation term with respect to the electric field perturbation, which is algebraically complicated and time consuming step in the completely analytic CPKS method. The NIA-CPKS approach gives single step solution to CPKS equations [38,131]. This approach is a combination of numerical and analytical procedures to obtain the electric response in terms of perturbed density matrix. Here the complicated iterative scheme to solve CPKS is avoided. This makes the method practical to use for large molecules and large basis sets. This approach can be used for closed shell case only. Within NIA-CPKS, the elements of the derivative KS matrix are computed as the difference between the elements of KS matrices calculated at suitably chosen electric field values around zero.

\[
K_{\mu\nu}^{(\lambda)} = \frac{K_{\mu\nu}(+\Delta F_{\lambda}) - K_{\mu\nu}(-\Delta F_{\lambda})}{2 \Delta F}
\]  

(1.45)

Here \(K_{\mu\nu}^{(\lambda)}\) is an element of the perturbed KS matrix in the atomic orbital basis. The values \(+\Delta F_{\lambda}\) and \(-\Delta F_{\lambda}\) in the parentheses denote the symmetrically chosen field value and \(\Delta F\) is the magnitude of the electric field. Using this perturbed KS matrix the derivative of molecular orbital coefficients \(\mathbf{c}^{(\lambda)}\) in terms of the atomic orbital
basis is obtained analytically by solving the CPKS equation in a single step. The coefficient derivative leads to the first order perturbed density matrix with the elements:

\[ P_{\mu\nu}^{(\lambda)} = 2 \sum_{i}^{\text{occ}} c_{\mu i}^{(\lambda)} c_{\nu i} + c_{\mu i} c_{\nu i} \]  

(1.46)

The NIA-CPKS for calculating dipole-polarizability has been implemented in 1.7 version of deMon2k programme. The method has been validated and tested for various exchange-correlation functionals and basis set by application to some interesting class of systems. [39,132,133].

1.7.2 Auxiliary density perturbation theory

ADPT is derived from self-consistent perturbation (SCP) theory [134, 142-147] in the framework of ADFT [124]. For calculation of linear response of KS matrix requires the knowledge of linear response of density matrix is required. For closed shell systems this matrix can be obtained from SCP theory as follows:

\[ P_{\mu\nu}^{(\lambda)} = \frac{\partial P_{\mu\nu}}{\partial \lambda} = 2 \sum_{i}^{\text{occ}} \sum_{a}^{\text{unocc}} \frac{K_{i a}^{(\lambda)} - \epsilon_i S_{i a}^{(\lambda)}}{\epsilon_i - \epsilon_a} (c_{\mu i} c_{\nu a} + c_{\mu a} c_{\nu i}) - \frac{1}{2} \sum_{\sigma,\tau} P_{\mu\sigma} s_{\sigma\tau}^{(\lambda)} P_{\tau\nu} \]  

(1.47)

The overlap matrix derivatives in equation (1.47) vanish in the case of perturbation independent basis and auxiliary functions discussed here, and the expression for the perturbed density matrix elements simplifies to,

\[ P_{\mu\nu}^{(\lambda)} = 2 \sum_{i}^{\text{occ}} \sum_{a}^{\text{unocc}} \frac{K_{i a}^{(\lambda)}}{\epsilon_i - \epsilon_a} (c_{\mu i} c_{\nu a} + c_{\mu a} c_{\nu i}) \]  

(1.48)

Here \( \lambda \) is the perturbation parameter which represents an electric field component in this case and \( \epsilon_i \) and \( \epsilon_a \) are orbital energies of the \( i^{\text{th}} \) occupied and \( a^{\text{th}} \) unoccupied orbitals. The superscript notation refers always to partial derivatives, \textit{i.e.} does not affect molecular orbital coefficients in molecular integral transformations. The perturbed KS matrix \( K_{i a}^{(\lambda)} \) is given in the molecular orbital representation as,

\[ K_{i a}^{(\lambda)} = \sum_{\mu,\nu} c_{\mu i} c_{\nu a} K_{\mu\nu}^{(\lambda)} \]  

(1.49)
with:

\[ K_{\mu\nu}^{(\lambda)} = H_{\mu\nu}^{(\lambda)} + \sum_k \langle \mu \nu \parallel k \rangle \left( x_k^{(\lambda)} + z_k^{(\lambda)} \right) \] (1.50)

The perturbed exchange-correlation coefficients are given by:

\[ z_k^{(\lambda)} = \sum_l \langle k \parallel l \rangle^{-1} \langle l | v_{xc}^{(\lambda)} (\tilde{\rho}) \rangle \] (1.51)

Since \( v_{xc}^{(\lambda)} (\tilde{\rho}) \) is a functional of the approximated density it follows:

\[ \langle l | v_{xc}^{(\lambda)} (\tilde{\rho}) \rangle = \int \int \langle l | \tilde{\rho} \rangle \frac{\delta^2 E_{xc}[\tilde{\rho}]}{\delta \tilde{\rho}(r) \delta \tilde{\rho}(r')} \, dr \, dr' \]
\[ = \sum_m \langle l | f_{xc}[\tilde{\rho}] | m \rangle \chi_m^{(\lambda)} \] (1.52)

Compared to the standard kernel of LCGTOs, the scaling of the ADPT kernel integrals is reduced by 2 orders of magnitude. The exchange-correlation kernel \( f_{xc}[\tilde{\rho}] \) is defined as the second derivative of the exchange-correlation energy:

\[ f_{xc}[\tilde{\rho}(r), \tilde{\rho}(r')] = \frac{\delta^2 E_{xc}[\tilde{\rho}]}{\delta \tilde{\rho}(r) \delta \tilde{\rho}(r')} \] (1.53)

For pure density functionals, the arguments of the approximated densities are collapsed. Thus we obtain [148]:

\[ f_{xc}[\tilde{\rho}(r), \tilde{\rho}(r')] = \frac{\delta^2 E_{xc}[\tilde{\rho}]}{\delta \tilde{\rho}(r) \delta \tilde{\rho}(r')} \delta(r - r') = \frac{\delta^2 E_{xc}[\tilde{\rho}]}{\delta \tilde{\rho}(r)^2} = \frac{\delta v_{xc}[\tilde{\rho}]}{\delta \tilde{\rho}(r)} \] (1.54)

The numerical calculation of the kernel matrix elements in ADFT is described in ref [40] . With the explicit form for the perturbed exchange-correlation fitting coefficients we can rewrite the perturbed Kohn-Sham matrix as:

\[ K_{\mu\nu}^{(\lambda)} = H_{\mu\nu}^{(\lambda)} + \sum_k \langle \mu \nu \parallel k \rangle x_k^{(\lambda)} + \sum_{k,l} \langle \mu \nu \parallel k \rangle F_{k,l} x_l^{(\lambda)} \] (1.55)

Where,

\[ F_{k,l} = \sum_m \langle k \parallel m \rangle^{-1} \langle m | f_{xc}[\tilde{\rho}] | l \rangle \] (1.56)

Inserting equation (1.55) via equation (1.49) into equation (1.48) yields an explicit expression for the perturbed density matrix in terms of the perturbed fitting
coefficients. On the other hand, the derivation of the fitting equation (1.38) itself, assuming perturbation independent basis and auxiliary functions yields:

\[
\sum_{\mu,\nu} \tilde{p}_{\mu\nu}^{(\lambda)} \langle \mu \nu \parallel \tilde{m} \rangle = \sum_k x_k^{(\lambda)} \langle k \parallel \tilde{m} \rangle
\]  (1.57)

By combining equation (1.48), (1.49), (1.48) and (1.50) we then find:

\[
\sum_{\mu,\nu} \tilde{p}_{\mu\nu}^{(\lambda)} \langle \mu \nu \parallel \tilde{m} \rangle = 4 \sum_{l} \sum_{a} \left( \tilde{m} \parallel i a \right) H_{i a}^{(\lambda)} + 4 \sum_{l} \sum_{a} \sum_{k} \left( \tilde{m} \parallel i a \right) \langle k \parallel \tilde{m} \rangle x_k^{(\lambda)} + 4 \sum_{l} \sum_{a} \sum_{k} \left( \tilde{m} \parallel i a \right) \langle k \parallel \tilde{m} \rangle F_{k,l}
\]  (1.58)

Thus the perturbed density can be eliminated and the response equation can be formulated solely in terms of the perturbed fitting coefficients. As a result the dimension of the corresponding equation system is dramatically reduced, namely to the number of auxiliary functions, and a direct, non-iterative, solution becomes feasible. Further notation can be simplified by introducing the perturbation independent Coulomb and exchange-correlation coupling matrices \( A \) and \( B \). Their elements are given by:

\[
A_{k,l} = \sum_{l} \sum_{a} \frac{\langle k \parallel i a \rangle \langle i a \parallel l \rangle}{\varepsilon_l - \varepsilon_a}
\]  (1.59)

\[
B_{k,l} = \sum_{l} \sum_{a} \sum_{m,n} \frac{\langle k \parallel i a \rangle \langle i a \parallel \tilde{m} \rangle}{\varepsilon_l - \varepsilon_a} \langle \tilde{m} \parallel n \rangle^{-1} \langle \tilde{m} \parallel f_{xc} [\tilde{\rho}] \parallel l \rangle = \sum_{m} A_{k,m} F_{\tilde{m}l}
\]  (1.60)

Similarly, we define the elements of the perturbation vector as:

\[
b_k^{(\lambda)} = \sum_{l} \sum_{a} \frac{\langle k \parallel i a \rangle H_{i a}^{(\lambda)}}{\varepsilon_l - \varepsilon_a}
\]  (1.61)

Inserting these quantities into equation (1.58) yields:

\[
(G - 4A - 4B) \mathbf{x}^{(\lambda)} = 4 \mathbf{b}^{(\lambda)}
\]  (1.62)
Note that the term in parentheses is perturbation independent and, thus need to be calculated only one time. We then find for the perturbed fitting coefficients [124]:

$$\mathbf{x}^{(3)} = 4 \mathbf{G}^{-1} \mathbf{b}^{(2)}$$

In the case of polarizability calculations three different perturbation vectors need to be calculated, each for one field component. Once a perturbed fitting coefficient vector is obtained it is inserted into equation (1.55) in order to obtain the corresponding perturbed Kohn-Sham matrix. With the perturbed Kohn-Sham matrix the perturbed density matrix is calculated via the SCP equation (1.48). Therefore, the final ADPT result is identical to the corresponding CPKS solution. The difference is the elimination of the perturbed density matrix from the response equation system in ADPT. As already discussed this is accompanied by a significant reduction of the dimensionality of this equation system and, thus permits direct, non-iterative, solutions. From the perturbed density matrix the polarizability tensor elements are calculated as:

$$\alpha_{\lambda\eta} = \sum_{\mu\nu} \mathbf{P}_{\mu\nu}^{(2)} \langle \mu | r_{\eta} \nu \rangle$$  \hspace{1cm} (1.64)$$

where $\lambda$ denotes the Cartesian component of the electric field and $\eta$ of the dipole moment integral.

1.8 Molecular dynamics methods

Molecular properties are very sensitive to the environment and the temperature. The effects of a finite temperature can be incorporated by means of the statistical mechanics methods. The representative samplings of the system are generated at finite temperature known as simulation. There are two major techniques for generating an ensemble namely Monte Carlo (MC) and molecular dynamics (MD). However, time-dependent phenomenon can be studied with molecular dynamic simulations. The method generates a series of time-correlated points in phase space (a trajectory) by propagating a starting set of coordinates and velocities according to Newton’s second equation by a series of finite time steps.
1.8.1 Classical molecular dynamics

The basic principle of classical molecular dynamic is that the nuclear motion in a molecular system is treated by the classical equations of motion. The forces on atoms are derived from classical potential such as Lennard–Jones, Buckingham, etc. These classical potentials do not describe the electronic motion and hence, classical MD becomes computationally much cheap. Here the successive configurations of the system are generated by integrating the Newton’s equation of motion. Thus the time correlation of positions and velocities of the atoms in the system can be explained. Hence, MD is a deterministic approach, in which the state of the system at any future time can be predicted from its current state [149].

The trajectory is obtained by solving the differential equations involved in the Newton’s second law. Given a set of atoms of masses \( M_i \) at position \( R_i \) one can write

\[
F_i = M_i \ddot{R}_i \quad (1.65)
\]

Where \( F_i \) is the force on atom I, which is related to the potential \( U(R_i) \) as

\[
F_i = -\frac{\partial U(R_i)}{\partial R_i} \quad (1.66)
\]

Velocity-Verlet algorithm is the most commonly used time integration algorithm in molecular dynamics methods to solve the above equations [149]. The basic idea is to write two third-order Taylor expansions for the position \( R_i(t) \), one forward and one backward in time. Adding these two equations gives a recipe for predicting the position a time step \( \Delta t \) later from the current and previous positions, and the current acceleration.

Acceleration can be calculated from force or equivalently, the potential. Velocities are needed to calculate kinetic energy, it can be calculated as

\[
V_i(t) = \frac{R_i(t + \Delta t) - R_i(t - \Delta t)}{2\Delta t} \quad (1.67)
\]

The velocities, forces and instantaneous values of all properties obtained after every \( \Delta t \) step is stored. This time ordered information can be used to calculate time correlation function, and thus can be used to calculate the transport properties such as diffusion coefficient, viscosity coefficient, etc. The temperature dependent properties can also be calculated from the equipartition law.
\[
\frac{3}{2} N K_B T = \left( \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 \right)
\] (1.68)

In classical MD it is difficult to account for the local atomic properties such as, chemical bonding, including the chemical reactions which form and break bonds in a quantum mechanical fashion. On the other hand, quantum dynamics of the nuclear motion of a large molecular system becomes highly computationally expensive. These difficulties can be accomplished by the use of \textit{ab initio} MD (AIMD).

### 1.8.2 \textit{Ab Initio} molecular dynamics

In AIMD, the motion of the individual atoms is simulated using forces which are calculated quantum mechanically [150, 151]. The nuclei are much heavier than the electrons, thus should be moved classically using the Newton’s equation of motion under the electronic potential derived from quantum mechanical approach. In 1985, in a seminal paper, Car and Parrinello initiated the field of AIMD by combining the conventional MD technique with the DFT and were termed to be CPMD [152]. Thus the study of formation and breaking of chemical bonds became possible, in contrast to the conventional MD. A number of other techniques have been developed which are based on minimization of the electronic orbitals to their ground state at each time step. These techniques were referred to as BOMD [153].

**Born-Oppenheimer molecular dynamics**

It is the most commonly applied approach to AIMD. The BOMD simulation solving the static electronic structure problem is solved in each molecular dynamics step, given the set of fixed nuclear positions at that instance of time [153]. Where the time-independent Shrödinger equation is solved and simultaneously nuclei are propagating through classical molecular dynamics. The electronic problem is solved using DFT for obtaining the ground state eigenvalue. For an interacting system of electrons with classical nuclei fixed at positions \( \{ R_N \} \), the total ground state energy can be found by minimizing the KS energy functional with respect to basis subject the orthonormality contrain. The corresponding Lagrangian for BOMD is given as

\[
\mathcal{L}_{BO}(R^N, \dot{R}_N) = \sum_{i=1}^{N} \frac{1}{2} M_i \dot{R}_i^2 - \min_{\{ \phi_{i} \}} E_{KS}[\{ \phi_{i} \}, R^N]
\] (1.69)
Equations of motion are given as

\[ M_i \ddot{R}_i = -\nabla_i \left[ \min_{\{\phi_i\}} E^{KS}[\{\phi_i\}, R^N] \right] \]  

(1.70)

The equation of motion ensures that the minimization of the electronic energy is done at each MD step.

1.9 Motivation and objectives of the thesis

In last few years electric response properties have been studied in great details for various systems due to its wide application in predicting various chemical phenomena. Along with its fundamental importance in understanding molecular interaction, it is understood that the spectroscopic measurements are dominated by polarizabilities. Dipole-quadrupole polarizabilities and their derivatives with Cartesian coordinates are important quantities in vibrational Raman optical activities (VROA). Also the nonlinear optical properties (NLO) such as hyperpolarizabilities are influential tools for designing newer and efficient NLO materials. The experimental methods are complicated and time consuming, thus the theoretical methods have played important role in calculating these properties with reasonable accuracy. Various theoretical methods have been developed for calculation of electric response properties. However, the available analytical methods cannot be applied to the metal clusters, bigger organic molecules along with large basis sets. The numerical methods can serve the purpose but one has to compromise with the accuracy. This has motivated us to develop a new numerical-analytical method for calculation of electric response properties.

The conventional CPKS approach of response calculation method is computationally expensive due to its iterative nature. The functional derivative of the exchange-correlation energy is the foremost bottle neck for building derivative Kohn-Sham matrix. Thus our formalism provides the major simplification to the CPKS approach. The calculation of perturbed KS matrix with finite-field method leads to single step solution to CPKS, thus the name NIA-CPKS. The method has been developed for studying electric properties of large molecules and basis sets with reasonable accuracy. In Chapter 2, we present the rigorous calculation of dipole-dipole polarizabilities of some push-pull systems with good basis set and its comparison with ADPT method. In this thesis we present the newer implementation of NIA-CPKS in SCP formalism within deMon2k. Technical details of the
implementation are presented in Chapter 3. There are fewer studies available for accurate and efficient calculation of dipole-quadrupole polarizabilities. The implementation of NIA-CPKS is further extended for calculation of dipole-quadrupole polarizabilities and applied for some interesting tetrahedral systems. The detailed discussion on dipole-quadrupole polarizabilities can be found in Chapter 4. In literature it has been seen that the temperature and frequency effects are important for dipole-quadrupole polarizabilities. Chapter 5 focuses on the study of dynamic dipole-quadrupole polarizabilities at elevated temperature. The calculations are performed using ADPT method along MD trajectories. In Chapter 6, we present the detail discussion on behaviour of dipole-dipole polarizabilities and dipole-quadrupole polarizabilities at stretched geometries. The major conclusions drawn from the present study and the future scope of the method are discussed in Chapter 7.
References:


64. Raimes, S. *Many-Electron Theory*, (North-Holland, Amsterdam, 1972)


85. Fermi, E.; *Z. Phys.* 1928, 48, 73.


