Study of Molecular Response Properties within Extended Coupled Cluster Framework

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in Physical Sciences

By

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I hereby declare that the work incorporated in this thesis entitled **"Study of Molecular Response Properties within Extended Coupled Cluster Framework"** submitted by me for the degree of Doctor of Phylosophy in Physical Sciences to the AcSIR is the record of the work I have carried out under the supervision of Dr. Nayana Vaval, is original and has not formed on the basis of award of any degree or diploma. Such material has been obtained from other sources has been duly acknowledged in this thesis.

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To my parents...

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Sayali P.Joshi

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Abstract

Molecular response properties can be viewed as derivative of the energy with respect to perturbation. These properties are calculated using numerical, analytical or semi numerical approach. In this thesis extended coupled cluster (ECC) method is used for the calculation of various properties of the molecules. The properties studied in this thesis are IR and Raman intensities, vibrational frequency, dipole moment, quadrupole moments and dipole-quadrupole polarizability. The non-iterative partial triples within ECC approach is used for the calculations of IR, Raman intensities and vibrational frequencies. We have also studied potential energy surface using decoupled approach within ECC method. The knowledge of gradient is essential for predicting precise values of various molecular properties. In studies of poly-atomic potential-energy surfaces, analytic gradient is necessary for locating extreme points. We have done formulation of analytic gradient within ECC framework.

Single reference coupled cluster method (SRCC) [1] has been established as the most accurate and efficient method for the calculation of molecular properties of the systems in their ground state. It provides the size-extensive energies and energy derivatives even in its approximate form. Due to this remarkable feature of the method, the SRCC is popularly used for studying energy as well as energy derivatives [2-5] of various closed shell molecular systems near equilibrium geometry. In most of the cases, restricted Hartree-Fock (RHF) is used as a reference wave function. The well-known and commonly used approach of the CC functional is non-variational CC.

The single reference coupled cluster response approach was first developed by Monkhorst *et. al.* [5]. Although energy derivative calculation can be done using SRCC method, it becomes complex due to absence of (2n+1) rule [6]. Within non- variational (NVCC) framework first derivative of energy requires first derivative of the wave function. This makes it very difficult to implement this method for geometric derivatives. To avoid the dependency of wave function derivatives, the Z-vector technique was introduced Handy and Schaefer [7] in context of analytic gradient within Configuration Interaction (CI). Bartlett and co-workers [8] implemented the Z -vector technique in CC approach. This method is simple for calculating first order derivatives, however, extending this method to higher order derivatives is cumbersome. Jorgensen and co-workers [4] proposed constrained variational approach (CVA) based on Lagrange's undetermined multipliers, which can be extended to higher order properties easily.

Stationary response or variational approach is another way of evaluating molecular properties. These methods follow Hellmann-Feynman theorem, i.e. (2n+1) [6] rule, that simplifies the calculation of energy and related properties. Choice of the energy functional is important for variational approach. In this approach energy functional is made stationary with respect to cluster amplitudes. Expectation value coupled cluster (XCC) [9], unitary coupled cluster (UCC) [10] and extended coupled cluster (ECC) [11] are the functionals which are normally used within coupled cluster framework. Among these XCC and UCC are studied in detail, but both are non-terminating series and give disconnected diagrams in the amplitude equations though energy functional is linked. On the other hand, ECC functional, due to double linking provides size extensive properties. Both the left and right operators are exponential in nature. The double linking form of the functional also ensures that the series is naturally terminating [12]. Though, the series is naturally terminating, the termination is at quite high order and needs truncation for practical application. Initial truncation was based on the number of cluster amplitudes in the energy functional. In the current implementation we have used the right amplitudes full exponential within singles and doubles approximation similar to the non-variational and all the complex conjugate double linked diagrams are included for left vector.

Chapter1**:** This chapter describes briefly various methods used in quantum chemistry for various calculations. The many body treatment for the electronic structure is described by the Hartree-Fock method. The Hartree-Fock method lacks the instantaneous repulsion i.e. dynamic correlation among electrons. To include this dynamic correlation, various theories like CI, perturbation are explained with their pros and cons. Coupled cluster theory and various developments involved in it are discussed in details. We discuss the extended coupled cluster (ECC) method in detail with the scope and objective.

Chapter2*:* This chapter explains the implementation of ECC to study the harmonic vibrational frequencies, infrared (IR) intensities, Raman intensities and depolarization ratio. Raman and IR intensities are mixed derivatives of energy with respect to the electric field and geometric perturbation whereas vibrational frequencies are derivatives with respect to geometry. We use semi-numerical approach to obtain these derivatives. We have studied the effect of electron correlation and basis set for the mentioned properties. We compare our results with non-variational coupled cluster and experimental results wherever available. We have studied HF, BH, CH+, CO and H_2CO molecules in different basis sets. For HF molecule benchmarking is done with full CI values and basis set convergence is studied for this molecule. Effect of triples is studied for all the molecules.

Chapter3**:** In this chapter, we have studied quadrupole moments, dipole-quadrupole polarizabilities and dipole polarizabilities using analytic extended coupled cluster response approach. In the current implementation of the functional we have included all the double linked terms within coupled cluster singles and doubles (CCSD) approximation. These terms will be important for the accurate description of properties at stretched geometries. We report the properties for carbon monoxide and hydrogen fluoride molecules, as a function of bond distance and compare our results for carbon monoxide with the full CI results. We have also reported the properties of methane, tetrafluoromethane, acetylene, difluoroacetylene, water and ammonia.

Chapter4*:* ECC method has been implemented extensively for the calculation of molecular properties. Chapter 4 deals with the potential energy surface (PES) study using coupled and decoupled approximation of ECC. Decoupled approach within ECC framework shows good convergence for all the systems studied. Coupled ECC and a decoupled approximation of ECC. HF, N_2 and C_2 are studied as test systems. N_2 and C_2 being doubly and triply bonded, are considered to be interesting systems for PES study. We compare our results with Full CI (FCI) results wherever available. Decoupled approach within ECC framework shows good convergence for all the molecules.

Chapter5: In this chapter, we explain the formulation of the analytic gradient using ECC approach. The coupled perturbed Hartree-Fock equation is used (CPHF) for the derivative calculation of the coefficient matrix and Fock matrix. ECC being variational, we do not require derivative cluster amplitudes for calculation of gradients. However, to obtain the relaxed density, we need to solve Z vector equation. One and Two particle density matrices are calculated and are back transformed to obtain in atomic basis. These densities in AO basis are then contracted with derivative Hamiltonian to acquire the gradient of energy. The final goal is to perform geometry optimization.

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List of Publications

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Chapter 1

Introduction

1.1 Introduction:

Molecular quantum mechanics has become an important as well as successful tool for accurate prediction of various molecular properties [1-6]. Electric properties such as dipole moment, polarizability, hyperpolarizability, quadrupole moment, dipole-quadrupole polarizability, magnetic properties like magnetizibility, Nuclear magnetic resonance (NMR) shifts, geometric properties such as vibrational frequencies and mixed properties like infrared intensities, Raman intensities play important role in determining the structure as well as interpreting characteristics of molecules. Electric properties are useful in designing nonlinear optical properties [7-11] while properties like dipole-quadrupole polarizability are important in prediction of Raman scattering spectra [12] and interaction induced light scattering spectra [13]. Magnetic properties such as NMR [14] are used for detecting the presence of particular nuclei in a compound along with prediction of chemical shift and coupling constant. Geometric properties like gradient help us in finding global minima, local minima on potential energy surface (PES). These properties related to PES are not direct observable but can be involved in reaction pathways. Transition states, chemical reaction dynamic and energy barriers are complex properties for studying but, the information related to these can be obtained with the geometric properties. Vibrational frequencies, i.e. second derivative of energy with respect to geometric perturbation predict the structural information. Theory and computational studies include several mathematical tools [15-16], which can build a model for predicting different properties of system, that are difficult to calculate experimentally. Successful prediction of these molecular properties depends on accuracy of the method used. Hence for the accurate prediction of electronic structure [17] there is need to go beyond mean- field approximation(HF) [5,18-21] *Ab-initio* methods, like Configuration Interaction (CI) [5,22-23], many body perturbation theory (MBPT) [24-26], Coupled Cluster Method (CC) [6,27-32], all consider Hartree-Fock (HF) single determinant as a reference function for the calculation of energy and properties of closed shell systems. The accuracy of the method is determined by the size consistency and size extensivity [5, 28, 33-34] the accuracy of method is determined.

Single reference coupled cluster method (SRCC), due to its success in its ability to provide accurate and size extensive values of energy and energy derivatives even in its approximate form, has evolved as a state of the art method [6,27-32]. Traditionally SRCC has been used in non-variational form. Requirement of wave function derivative for the calculation of energy derivative was the biggest impediment in its wider applicability. Implementation of Z-vector method makes the problem solving easier [35-37]. However, it is complicated to extend this approach for higher order derivatives. Constrained variational Approach [38] on the other hand can be easily extended for higher derivatives.

An alternative approach for evaluation of energy and properties is a fully variational or stationary approach, in which energy functional is defined, that is made stationary with respect to parameters in it. Being variational, the method satisfies Hellmann-Feynman theorem, which makes it suitable for the calculation of energy derivatives. Expectation value coupled cluster (XCC) [39], unitary coupled cluster (UCC) [40] and extended coupled cluster (ECC) [41] are variational approaches documented in literature.

The inefficiency of the SRCC method in explaining the bond dissociation of molecule motivated the formulation of variational response approaches for PES calculations. Pal and co-workers have extensively used ECC method for calculation of electric [42] as well as for magnetic properties [43, 44]. The present thesis uses ECC method for calculation of molecular properties. In the second chapter, we have computed Infrared intensities (IR) and Raman intensities along with vibrational frequencies deploying semi-numerical approach. Partial triples excitation in non-iterative manner is implemented along with singles and doubles excitation (ECCSD) within ECC framework. The third chapter provides the calculation of electric properties such as dipole polarizability, dipole-quadrupole polarizability using ECC approach wherein comparison of cubic truncation and full ECCSD method for hydrogen fluoride as well as carbon monoxide molecule have been done. Apart from these, calculation of properties for methane, tetrafluoromethane, acetylene, difluoroacetylene, water and ammonia has been evaluated. Decoupled approximation within ECC method has been implemented for the calculation of PES in and covered in chapter four. The coupled ECC due to double number of equations gives the convergence problem near bond dissociation limit. Both coupled and decoupled approaches are reported for the PES calculation for the comparison. There is importance of analytic gradients, for determining various properties accurately and precisely, the formulation of gradients within ECC framework is described in detail in chapter five. The Chapter 6 gives the summary of the thesis.

1.2 Quantum mechanical view towards atoms and molecules

The base of any substance constitute of atoms and molecules, these consists of positively charged nuclei and negatively charged electrons revolving around, which form a strong repulsive force among them, while a strong attractive force with the nuclei. Atom can be defined as species having one nucleus while molecules consist of two or more than two nuclei.

We can study the electronic structure of atoms and molecules by solving non-relativistic time-independent Schrödinger equation [4, 5].

$$H\Psi = E\Psi \tag{1.1}$$

Here in equation (1.1), $\hat{H}$ describes the Hamiltonian operator for the calculation of total energy of the system. Ψ defines the wave function on which the Hamiltonian operates to give the eigen values. Hamiltonian operator consists of kinetic energy of individual particle and potential energy arising because of attraction and repulsion between the constituting particles. Complicated interaction with surroundings may contain the effect of external electric as well as magnetic field. When there is no external field, Kinetic and potential energy are the dominant contributors to the Hamiltonian. The kinetic energy is composed of electronic and nuclear part, while the potential energy can be written as sum of electron nuclear attraction, nuclear-nuclear repulsion and electron-electron repulsion energy terms respectively. Thus the Hamiltonian containing N electron system can be written as [5]

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \tag{1.2}$$

Here,

$$\hat{T}_n = -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2; \; \hat{T}_e = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2; \; \hat{V}_{nn} = +\sum_{A=2}^{M} \sum_{B=1}^{A-1} \frac{Z_A Z_B}{\left\| \vec{R}_A - \vec{R}_B \right\|};$$

$$\hat{V}_{ne} = -\sum_{A=1}^{M} \sum_{i=1}^{N} \frac{Z_A}{\left\| \vec{r}_i - \vec{R}_A \right\|}; \; \hat{V}_{ee} = +\sum_{i=2}^{N} \sum_{j=1}^{i-1} \frac{1}{\left\| \vec{r}_i - \vec{r}_j \right\|}; \tag{1.3}$$

In equation (1.3), $\vec{R}_A$ represents the spatial coordinate of Ath nuclei while $\vec{r}_i$ represents the spatial coordinate of ith electron.

An orbital can be described as one particle wave function.

$$\boldsymbol{\Psi} = \left(\mathrm{R}_1, \mathrm{R}_2, ..., R_m, x_1, x_2, ..., x_n \right) \tag{1.4}$$

Any N-electron wave-function can be expanded as a linear combination of N-one electron anti-symmetric functions. Though the N-electron function contains complicated structure, it can be written as product of N-one electron functions those are basically the orbitals. Determinant is used for introducing the anti-symmetry instead of simple product of orbitals.

Such determinants are known as Slater Determinants [19], they can be written as,

$$\Psi(x_1, x_2, .., x_N) = (N!)^{-1/2} \left\| \chi_i(x_1), \chi_j(x_2), .., \chi_k(x_N) \right\| \tag{1.5}$$

Here χ_i 's represent the spin orbitals. In equation (1.5), the electrons are represented by rows while that of spin orbitals are represented by columns. As mentioned earlier Slater determinants take care of anti-symmetry and thus Pauli exclusion principle is automatically obeyed. Thus no two electrons with the parallel spin can be in one orbital. This concept is known as Fermi hole. The origin of Fermi hole is from Fermi-Dirac statistics. Other concept namely Coulomb hole, which is the result of coulombic repulsion between electrons signifies that, the probability of finding two electrons at the same point in space is zero. Although, an arbitrary antisymmetric wavefunction does not ensure Coulomb hole, but the anti-symmetry takes care of the Fermi hole. However, there is existence of Coulomb hole in the Fermi hole to some extent.

Equation (1.1) provides the solution of eigen value problem that results into stationary state energies and corresponding eigen-functions. Solving equation (1.2) is difficult, since it contains complex terms. However, according to the Born- Oppenheimer approximation (BOA), which assumes, the nuclei being heavier than electrons, their motion is slow and hence their motion can be considered as stationary compared to the motion of electrons. Thus BOA simplifies the complex Hamiltonian into simpler one by neglecting the kinetic energy and the nuclear-nuclear repulsion term is treated as a constant. As any constant added to an operator just adds to eigenvalues and thus it does not affect the eigenfunction of the operator. This simplified electronic Hamiltonian thus contains the kinetic part of electrons, electron nuclear attraction and electron-electron repulsion. The electronic Hamiltonian can now be written as,

$$\hat{H}_{ele} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\sum_{i=1}^{N}\frac{Z_A}{\left\|\vec{r}_i - \vec{R}_A\right\|} + \sum_{i=2}^{N}\sum_{j=1}^{i-1}\frac{1}{\left\|\vec{r}_i - \vec{r}_j\right\|} \tag{1.6}$$

Sutckiffe [45] pointed out the quantitative aspects including the corrections to BOA. The electronic Hamiltonian gives eigenvalues that result into total electronic energies of the corresponding stationary states. The parameters of eigenfunction are dependent on nuclear co-ordinates. The nuclear-nuclear repulsion energy added to electronic energy results into potential energy surface (PES). Thus the BOA helps in simplifying the complex problem that involves several nuclei and electrons to an at least many-electron problem at given fixed geometry.

1.3 Approximate theories for solving molecular structure problem:

However, solving equation (1.6) is quite difficult even for small systems. BOA for many electron systems is still complicated to solve. The bottleneck lies in the electron-electron repulsion term $\hat{V}_{ee}$ in the electronic Hamiltonian explained in equation (1.3). Due to electron-electron repulsion term equation (1.6) cannot be solved exactly. One has to make further approximations to solve the Hamiltonian equation given by (1.6) ensuring accuracy in qualitative as well as in quantitative manner. For the method to be considered a theoretical model for calculating electronic energies and properties, there are some basic conditions that method must fulfil at all stages initially proposed by Pople *et. al*. [33]and further collectively stated by Bartlett *et.al.*[28], though it can be improved in a systematic way. Some of requirements for the method can be listed here as

1. The specific method should be applicable to a wide range of molecular system. It should not be confined to certain choices of configuration and symmetry.
2. The method should be consistent with different class of transformation. Specifically, the unitary transformations should not change the orbital energy degeneracy and the related effects.
3. **Size-consistency** is one of the main necessity of the method. The phenomenon of size-consistency can be explained as, when the big molecule is dissociated of into its fragments; total energy of the molecule should be equal to the individual energies of its fragments separated at an infinite distance.
4. **Size-extensivity** is an important criterion that a method should serve. It can be described as the energy of a strongly interacting many electron system for a given potential should be proportional to number of electrons in the system.
5. However, may the theory is precise in explaining the treatment to electronic structure; the method should be feasible computationally to be applicable to molecular systems. As the chemical systems are large in size.
6. For open-shell systems and excited states the method should be applicable.

1.4 Hartree-Fock Theory:

Perceiving and explaining the approximate solutions of Schrödinger equation has been a very important concern for all quantum chemists. In the absence of electron-electron repulsion term, the electronic Hamiltonian can be exactly solved i.e. just calculating each term separately and adding them to get final electronic energy. However in reality, the $\hat{V}_{ee}$ i.e. electron-electron repulsion term is always present and is the most time consuming as well as tricky term. However, Hartree-Fock is the best possible single determinant. Spherical averaging of electronic-electronic interaction gives the best solution for the class of simple independent particle model wavefunction. The gist of Hartree-Fock [5,18-19] approximation is to replace the complicated many-electron problem by one-electron problem in which electron-electron repulsion is treated in an average way. According to the variation principle the best wavefunction is one, which gives minimum energy. Thus the form can be written as,

$$E_0 \leq \left\langle \Psi_0 \middle| \hat{H}_{ele} \middle| \Psi_0 \right\rangle \tag{1.7}$$

Wavefunction representing the spin orbitals is thus optimized using variational theorem. Hence using this, resultant HF equation is obtained, which is further solved iteratively.

The Fock operator $\hat{f}$ is defined as,

$$\hat{f}(i) = h(i) + v^{HF}(i) \tag{1.8}$$

Where $\hat{f}$ [5] is the addition of core-Hamiltonian operator $h(i)$ and an effective one-electron potential operator that is called as Hartree-Fock potential $v^{HF}(i)$.

Thus Hartree-Fock equation becomes,

$$\hat{f}(i)\chi_a(\vec{x}_i) = \varepsilon_a \chi_a(\vec{x}_i) \tag{1.9}$$

The core-Hamiltonian term can be written as,

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} \tag{1.10}$$

$$v^{HF}(\vec{x}) = \sum_{b=1}^{N} J_b(\vec{x}) - \sum_{b=1}^{N} K_b(\vec{x}) \tag{1.11}$$

where $v^{HF}(i)$ is the average potential experienced by ith electron due to the presence of other electrons. This potential depends on the spin orbitals of the other electrons, thus Fock operator depends on its eigenfunction.

$$J_b(\vec{x})\chi_a(\vec{x}) = \int dx' \frac{\chi_b^*(\vec{x}')\chi_b(\vec{x}')}{|\vec{x}-\vec{x}'|}\chi_a(\vec{x}) \tag{1.12}$$

$$K_b(\vec{x})\chi_a(\vec{x}) = \int dx' \frac{\chi_b^*(\vec{x}')\chi_a(\vec{x}')}{|\vec{x}-\vec{x}'|}\chi_b(\vec{x}) \tag{1.13}$$

Thus equation (1.12) describes the effective two electron potential, which is sum of average Coulomb interaction by local operator $J_b(\vec{x})$ as well as a non-classical potential represented by an non-local exchange operator $K_b(\vec{x})$. By substituting the Coulomb and exchange operators the final non- canonical form of the Fock operator can be obtained. Thus canonical Hartree-Fock equation can be obtained by using an unitary transformation. It signifies that if we start with a set of spin orbitals $\{\chi_a\}$ of orthonormal spin orbitals, the new set $\{\chi'_a\}$ will also be orthonormal. Thus for an N-electron system the Fock operator has a functional dependence on the occupied spin orbitals, but once the occupied spin orbitals are known, the Fock-operator becomes as well defined Hermitian operator, which will have an infinite number of eigenfunctions.

$$f\left|\chi_j\right\rangle = \varepsilon_j\left|\chi_j\right\rangle \qquad j = 1, 2, ...\infty \tag{1.14}$$

$$E_0 = \sum_{a}^{N}\langle a|h|a\rangle + \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N}\langle ab\|ab\rangle \tag{1.15}$$

Thus,

$$E_0 \neq \sum_{a}^{N} \varepsilon_a \tag{1.16}$$

Total ground state energy is not the sum of orbital energies. The cause for this is, the energy ε_a includes coulomb and exchange interactions between electron in $\{\chi_a\}$ and electrons in all other occupied spin orbitals in specific $\{\chi_b\}$. Similarly ε_b also includes coulomb and exchange interactions between an electron in $\{\chi_b\}$ and electrons in all other occupied orbitals in particular $\{\chi_a\}$. Thus addition of ε_a and ε_b includes the electron-electron interaction twice. Thus $\frac{1}{2}$ factor needs to be included in the corrected expression. Using Roothan equations [20] we get the Fock operator that can now be written in the form of matrix

$$FC = SC\varepsilon \tag{1.17}$$

Thus Hartree- Fock equation is solved in an iterative manner. The procedure to solve this equation is called self-consistent field (SCF) method [46]. To solve the equation, one should make an initial guess of spin orbitals; also the average field seen by each electron can be calculated. Then the eigen value equation can be solved for a new set of spin orbitals. This procedure is repeated until the Self consistency is achieved i.e. until there is no longer change in field and the spin orbitals used to construct the Fock operator are same as its eigenfunction. Hartree-Fock eigenvalue equation produces a set of orthonormal spin orbitals with orbital energies $\{\varepsilon_k\}$. The N spin orbitals with lowest energies are called occupied orbitals and rest of the remaining orbitals $\{\chi_k\}$ are termed as unoccupied or virtual orbitals. Koopmans' theorem provides the physical significance of orbital energies and states that the energy of an occupied orbital in HF ground state is negative of energy required for removing an electron from the orbital without relaxation of the rest of the orbitals. Ionization potential is therefore better explained by Koopmans' approximation rather than electron affinities.

Using this HF approximation for closed shell molecules, where the spin part of the orbital is balance with spin-up and spin-down part. Further using Roothan-Hall equation for integrating these spin orbitals to get the spatial orbitals is thus well known as restricted HF (RHF). Similarly for open shell systems, those with maximum number of orbitals filled can be solved with restricted open shell HF (ROHF). However for some systems the occupancy of electron is not considered as an important factor to solve HF equations, such equations are termed as unrestricted HF (UHF) and these further lead to Popel-Nesbet equations.

The HF single determinant is best approximation to ground state. But in real systems there may exist determinants those are singly excited. The Brillouin's theorem [5] say's that, there will be no interaction between the HF determinant and singly excited determinant.

$$\left\langle \Psi_0 \middle| H \middle| \Psi_i^a \right\rangle = 0 \tag{1.18}$$

The HF approximation thus gives the energy which is 99 % accurate. However, for the real application like reaction mechanics, transition states the energy difference is important. This small difference called as electron correlation effect is missing in HF due to its consideration as mean field approximation. The electron correlation is difference between exact energy and HF energy. Hence we need to search further for other approximate theories which are more accurate in terms of predicting electron correlation. Such methods are generally known as many body theories. Although HF approximation lacks the instant dynamic correlation i.e. electron correlation, mostly it is used as starting guess for the calculations.

1.5 Second Quantization

Slater determinants [19] fulfil the criteria for anti-symmetry principle. However, dealing with the huge determinants for larger systems becomes very tedious for calculation since there is dependency on number of electrons. To overcome this problem, a method known as second quantization is used. The method takes care of anti-symmetry property of wavefunction by transferring it onto algebraic properties of certain operators without introducing any new physics. Rather second quantization is an elegant way of treating many-electron systems with one- and two-electron integrals instead of N-electron wavefunction [5]. These algebraic operators are termed as creation operators and annihilation operators. As the names suggest creation operator creates an electron in a spin orbital, while an annihilation operator removes an electron from the spin orbital. Creation operator $a_i^\dagger$ operates on vacuum to create an electron i in a spin orbital χ_i.

$$a_i^\dagger \left| \chi_k \cdots \chi_l \right\rangle = \left| \chi_i \chi_k \cdots \chi_l \right\rangle \tag{1.19}$$

Similarly an annihilation operator a_i destroys i$^{\text{th}}$ electron from the spin orbital.

$$a_i \left| \chi_i \chi_k \cdots \chi_l \right\rangle = \left| \chi_k \cdots \chi_l \right\rangle \tag{1.20}$$

However, the Slater determinants obtained either from creation or annihilation operators should satisfy the anti-symmetry principle.

$$a_i^\dagger a_j^\dagger \left| \chi_k \cdots \chi_l \right\rangle = a_i^\dagger \left| \chi_j \chi_k \cdots \chi_l \right\rangle = \left| \chi_i \chi_j \chi_k \cdots \chi_l \right\rangle \tag{1.21}$$

$$a_j^\dagger a_i^\dagger \left| \chi_k \cdots \chi_l \right\rangle = a_j^\dagger \left| \chi_i \chi_k \cdots \chi_l \right\rangle = \left| \chi_j \chi_i \chi_k \cdots \chi_l \right\rangle = -\left| \chi_i \chi_j \chi_k \cdots \chi_l \right\rangle \tag{1.22}$$

Creation operator cannot create an electron in a spin orbital, if electron is already present. Similarly annihilation operator cannot destroy an electron if it is not present in the orbital. Thus a vacuum is a state that can be defined as absence of electrons and is represented as $(\left| \ \right\rangle or \left| \ \right\rangle)$. These operators obey the anti-commutation relation among them.

$$\begin{aligned} \left\{ a_i^\dagger, a_j^\dagger \right\} &= a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 \\ \left\{ a_i, a_j \right\} &= a_i a_j + a_j a_i = 0 \\ \left\{ a_i^\dagger, a_j \right\} &= a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij} \end{aligned} \tag{1.23}$$

From equation (1.22) and (1.23) we can conclude that interchanging between any two creation or annihilation operators will result in change in the sign of determinant and hence the anti-symmetry principle is satisfied. Electronic Hamiltonian thus can be written in second quantised form,

$$\hat{H}_{ele} = \sum_{i,j} \langle i | \hat{h} | j \rangle a_i^\dagger a_j + \frac{1}{2} \sum_{i,j,k,l} \langle ij | \frac{1}{\hat{r}_{12}} | kl \rangle a_i^\dagger a_j^\dagger a_k a_l \tag{1.24}$$

Due to annihilation operator acting on vacuum, the result is zero and hence the arrangement of creation and annihilation operators has to be made in such way that annihilation operators are to the right of creation operator. This terminology is known as normal ordering. Using normal ordering along with Wick's theorem [24, 47-48], tedious algebra can be made simpler also the physics can be easily understandable.

1.5.1 Concept of hole and particle:

The algebra obtained using second-quantization can be further simplified i.e. some reference configuration is considered for occupancy. This reference configuration is generally specified as an occupied orbital for the presence of electrons, while the unoccupied orbitals are termed as virtual orbitals. Thus the concept of hole and particle is introduced and replaces electrons for solving algebra. The annihilation of electron in an occupied orbital result in creation of hole while annihilation of hole in occupied orbital results in creation of particle in virtual orbital. This particle and hole formation can be represented diagrammatically. This diagrammatic technique was first time introduced by Richard Feynman [49] in context with quantum electrodynamics. Goldstone [50] used the technique for solving algebraic equations for perturbation theory. The diagrams are drawn using vertex, which represents the Hamiltonian. The downward arrow from one vertex to other shows internal hole line while upward arrow represents a particle line. Creation and annihilation of hole is represented by an inward and outward line while particle creation and annihilation is shown as an outward and inward line.

1.6 Different Correlated Methods Available in the Literature

For proper introduction of electron correlation different methods are available in literature. They are listed in terms of their accuracy in predicting electron correlation.

1. Configuration Interaction (CI).
2. Many Body Perturbation Theory (MBPT).
3. Independent Electron Pair Approximation (IEPA).
4. Coupled Electron Pair Approximation (CEPA).
5. Coupled Cluster Approximation (CCA).

All these methods contain some or the other level of truncation such as, truncated CI, finite order MBPT such as MP2, MP3, etc. and different electron pair approximation along with various truncations incorporated in coupled cluster approach. Each of the method has its pros and cons depending on the defined problem.

1.6.1 Configuration Interaction Method

Hartree-Fock approximation is a phenomenally successful in many of the systems since it is a best single determinant form of exact wavefunction, but has some of its limitations. Thus, this single determinant does take care of parallel spin but cannot treat the instantaneous repulsion i.e. dynamic correlation between two electrons between anti parallel spins. Thus HF theory is unable to explain the very small energy differences that matter qualitatively and also fails in explaining most of the chemical phenomenon like binding energy, excitation energy, activation energy, etc. that need energy differences rather than absolute energy.

Among all methods, Configuration Interaction (CI) [5, 22, 23] method is conceptually easy to understand i.e.; CI is most simple method to improve the wavefunction. Particularly CI represents a wave function as a linear combination of N-electron trial functions and use linear variational method for determination of coefficients. On the whole, it yields an exact solution of many-electron problem for ground as well as excited state of systems, provided the bases set are complete. The inclusion of all possible configurations of determinants is thus termed as Full CI (FCI) method. The coefficients of configurations can be variationally optimized to minimize the total energy of the system. However, in real systems there is a restriction for handling complete set of N-electron trial functions. That is if we have set of 2K one-electron spin-orbitals, with which $\begin{pmatrix} 2K \\ N \end{pmatrix}$ different N-electron Slater determinants can be constructed. Also for small molecules and moderate size one-electron basis sets, the number of N-electron determinants is huge. For a finite one-electron basis, there should be a truncation on trial function in some way and should use a fraction of all possible N-electron functions.

$$\boldsymbol{\Phi}_0 = c_0 \left| \boldsymbol{\Psi}_0 \right\rangle + \sum_{i \in occ} \sum_{a \in virt} c_i^a \left| \boldsymbol{\Psi}_i^a \right\rangle + \left(\frac{1}{2!} \right)^2 \sum_{i,j \in occ} \sum_{a,b \in virt} c_{ij}^{ab} \left\langle \boldsymbol{\Psi}_{ij}^{ab} \right| + \ldots. \tag{1.25}$$

In equation (1.25), the factor ensures that each determinant is counted once only. The $\boldsymbol{\Psi}_i^a$ represents the singly excited determinant formed from excitation of electron from ith orbital i.e. occupied orbital in HF determinant to athi.e. virtual orbital. In similar manner $\boldsymbol{\Psi}_{ij}^{ab}$ indicates the doubly excited determinant obtained by exciting the electrons from ith and jth orbitals to ath and bth orbitals respectively. We can find corresponding energies by using linear variation method. This consists of forming matrix representation of Hamiltonian in the basis of the N-electron functions of expansion and then the eigenvalues of matrix are found out. This matrix is termed as FCI matrix and corresponding method is called as FCI. Due to its variational nature the lowest eigenvalue will be upper bound to the ground state energy of the system, while the higher eigenvalues will be upper bounds to the excited states of the system. The wavefunction of CI can be written in intermediate normalized form, where the coefficient c_0 of wavefunction$\left| \boldsymbol{\Psi}_0 \right\rangle$ is very large than other excitations.

$$\left\langle \boldsymbol{\Psi}_0 \middle| \boldsymbol{\Phi}_0 \right\rangle = 1 \tag{1.26}$$

Using the property of intermediate normalization we can normalize exact ground state wave function $\left| \boldsymbol{\Phi}_0 \right\rangle$ for CI. The importance of this intermediate normalization is, it couples the coefficients of singles, doubles and triples. The set of all such equations form a large matrix, which has to be further diagonalized to obtain the correlation energy.

Although the FCI is theoretically perfect model, it does not satisfy the criteria of cost-effectiveness. Hence with the increasing number of electrons i.e. dimension of wavefunction and the increasing basis functions FCI becomes unsustainable even for small molecules with moderate size basis set. For practical application FCI is not feasible and has to be truncated. Ground state of wavefunction is not improved by just adding singly excited configuration, due to Brillouin's theorem [5], however doubly excited configuration also known as CI doubles (CID) improves the wavefunction to recover most of the correlation energy.

One-electron operator plays dominant role in defining the molecular properties like dipole moment, polarizabilities, etc. Therefore addition of singly excited determinants to doubly excited one is required. This method is popularly known as CI singles and doubles (CISD) and thus it describes one electron properties more accurately. However, the singly excited determinants do not directly interact with HF, they only interact through doubly excited determinants and thus the correlation energy is improved. To get more accurate correlation energy the higher excitations has to be added and those are termed as CISD (T), CISDT, and CISDTQ and so on.

As mentioned earlier the FCI is not possible practically even for moderate systems and hence one has to truncate the wavefunction. The essential requirement from a model system is, it should be size-consistent, and however, truncated CI does not satisfy the size-consistency as well as size-extensivity of the wave function, where the phenomenon of size-consistency is related to proper description of system at dissociation limit while size-extensivity defines the proper scaling of energy with number of electrons. Thus, truncated CI is not considered as a theoretical model.

1.6.2 Many Body Perturbation theory

Many Body Perturbation Theory (MBPT) [25, 26] is a systematic procedure to improve correlation energy. The method is not variational in nature; however, it is size consistent at each level of perturbation. Perturbation series can be subdivided into Rayleigh Schrodinger (RSPT)[24,25,51] and Brillouin Winger perturbation theory (BWPT) [24]. Using BWPT the energy obtained at each perturbation order depends on energy itself, thus an iterative procedure is adopted to solve for energy, however, energy obtained at higher order at each successive iteration is not size-extensive. Hence BWPT is not followed for obtaining correlation energy. In RSPT, depending on partitioning pattern of Hamiltonian there are two different perturbation theories namely Møller-Plessette (MP) and Epstein Nesbet (EN) namely. Thus the MP perturbation expansion is size consistent irrespective of order of perturbation where it gets terminated. K.A. Brueckner [51] first studied and proved that, for first few orders, some of the ill-behaved terms cancel and thus MBPT is size-consistent at each order. However, he could not prove the size-consistency for higher order terms. Goldstone [50] tried the diagrammatic technique for the algebraic expression in RSPT. Diagrammatically he found that the disconnected pieces represent the ill-behaved terms and are not linked. Such terms cancel at each order. This concept of linked and unlinked terms is obtained from the linked cluster theorem, which states that perturbation expansion of energy of many–body system can be represented uniquely by linked diagrams. This diagrammatic technique was first applied by Kelly [53] to obtain the correlation energy. Due to this spatial feature of the method it is studied in detailed in literature.

The Hamiltonian of the system can be written in the form of

$$H = H_0 + \lambda v \tag{1.27}$$

The Hamiltonian in MBPT can be split into a known part and unknown part. The known part gives major contribution of energy and is entitled as zeroth order Hamiltonian and is denoted as $\hat{H}_0$. Thus the eigenfunctions $\left\{\boldsymbol{\Psi}_i^0\right\}$ of $\hat{H}_0$ form a complete set with the corresponding eigenvalues denoted by E_i^0. The weakly interacting part is known as perturbation and is denoted by v and the exact energy can be expressed as an infinite sum of contributions of increasing complexity.

The equation contains eigenvalues of $\hat{H}_0$ and matrix elements of perturbation between the eigenfunctions of $\hat{H}_0$. All the terms that include products of n such matrix elements are grouped together and they constitute nth order perturbation theory.

$$\begin{aligned} \boldsymbol{\Psi}_i &= \boldsymbol{\Psi}_i^0 + \lambda \boldsymbol{\Psi}_i^1 + \frac{\lambda^2}{2!}\boldsymbol{\Psi}_i^2 + \frac{\lambda^3}{3!}\boldsymbol{\Psi}_i^3 + \dots. \\ E_i &= E_i^0 + \lambda E_i^1 + \frac{\lambda^2}{2!}E_i^2 + \frac{\lambda^3}{3!}E_i^3 + \dots. \end{aligned} \tag{1.28}$$

Here λ is the perturbation parameter, when $\lambda = 0$ corresponds to unperturbed Hamiltonian $\hat{H}_0$. When $\lambda = 1$, the system is completely perturbed corresponding to stationary states of exact Hamiltonian. Thus the exact states are obtained by carrying out Taylor series expansion the quantities around $\lambda = 0$.

$$E_i^{(1)} = \langle \Psi_i | V | \Psi_i \rangle \tag{1.29}$$

$$E_i^{(2)} = \sum_{n \neq i} \frac{\left| \langle \Psi_i | V | \Psi_n \rangle \right|^2}{E_i^{(0)} - E_n^{(0)}} \tag{1.30}$$

Equation (1.29) and (1.30) represent the first and second order correction to energy. Though first order correction does not improve the correlation energy, second order energy shows improvement in the correlation energy. Second order correction is also known as MP2.

Generally, MBPT can be used for any stationary state. Although most of the time it is used for ground state calculations. The accuracy of many body methods can be measured in terms of perturbation order. Especially MP2, MP3, etc, are very popular methods for their accuracy and relative simplicity.

1.6.3 Independent Electron Pair Approximation

If each pair of electrons is treated independent of other pairs then N-electron problem is reduced to N*(N-1)/2 electron pairs. Study of Pair theories [54] is important in calculating correlation energies. Due to Pauli's exclusion principle and two particle nature of Hamiltonian, electron pair theories give good sight of approximation for N electron atomic and molecular orbital. This approximation considers only one pair of electron at a time i.e. the approximation neglects pair coupling terms also IEPA consider cancellation of nonlinear terms with the terms present in energy. Hence interaction among the pairs is neglected. The total correlation energy can be represented as sum of pair contribution; those are obtained independently by solving effective two electron equations. The separation of pairs is termed as independent electron pair approximation (IEPA). The approximation was developed by Sinanoğlu [3] and Nesbet [54] independently. Different formulations were used by both the authors. Sinanoğlu termed the theory as Many-Electron Theory (MET) while Bethe-Goldstone Theory name was used by Nesbet. Freed and Robb [55] studied in detail about the relation between IEPA and perturbation method. The IEPA wave function for ijth pair may be written as

$$\boldsymbol{\Psi}_{ij} = \boldsymbol{\Phi}_0 + \sum_{a \prec b} C_{ij}^{ab} \left| \boldsymbol{\Phi}_{ij}^{ab} \right\rangle \tag{1.31}$$

Here i, j are occupied orbitals while a, b are virtual orbitals in the HF determinant. Linear variation is done to calculate the energy E_{ij} which is a sum of HF energy and pair correlation energy corresponding to pair ij.

The total correlation energy in IEPA approximation is defined as

$$E_{corr}^{IEPA} = \sum_{i<j} e_{ij}^{IEPA} \tag{1.32}$$

Despite of the fact that, the correlation energy for each pair is obtained through linear variation method; the sum of all is not upper bound to the exact correlation energy. Computationally, calculating IEPA is very similar to DCI for each pair separately and hence it is also termed as “pair-at-a-time” CI. However, the individual pair CI matrices are much smaller in size than DCI. The advantage of IEPA over DCI is, it is size-consistent. However, IEPA has a disadvantage that, it is not invariant to unitary transformations of occupied spin orbitals in HF determinant.

1.6.4 Coupled electron pair approximation

If the interaction between two pairs of electrons is assumed, then such interactions are known as coupled pair approximations. W. Meyer [56] proposed a series of schemes that assuming the coupling between the pairs. Among these schemes, some schemes perform in better way to give size-extensive results. Although Coupled electron pair approximation (CEPA) considers interaction among the pairs that is conceptually neglected in IEPA, it neglects most of the nonlinear terms that are included in more advanced approximation known as coupled-cluster approximation. Various versions of CEPA are known in literature.[17, 56, 57]. This approximation show very similar nature to some approximate versions of CI along with non-variational and non-perturbative coupled cluster approximation.

1.6.5 Coupled Cluster Approximation

Coupled cluster (CC) theories are most popular once due to their accuracy in predicting electron correlation. Sinanoğlu [3] and Nesbet [54] proposed and studied pair theories and these pair theories are considered as pioneer's for the formulation of CC. The form of wave function can be described as an exponential operator operating on suitable reference space, generally Hartree-Fock wave function. Cöester and Kümmel [58] used the cumulant expansion in nuclear physics to solve the atomic problems. This concept of cluster expansion was originated in statistical mechanics and are well known as Ursell and Mayer [59] expansion.Čižek and Paldus[60] first introduced the concept of CC in quantum chemistry, i.e. they derived the equations related to atomic problems. We can relate between coupled cluster approximation (CCA) and MBPT as, CCA can be written as infinite order of systematic summation selected class of MBPT diagrams. If a quantity A associated with a N-particle system is additively separable, then exp(A) can be shown as multiplicatively separable. Also it is mandatory for A to have contributions only from linked cluster to be additively separable.

Coupled cluster approximation (CCA) in the ground state wave function of N-electron systems is obtained by action of exponential wave-operator acting on HF as a reference function

$$\left|\boldsymbol{\Psi}_0\right\rangle = e^T \left|\boldsymbol{\Phi}_0\right\rangle \tag{1.33}$$

Here T defines basic linked excitation operator and if it includes all basic excitations of T, then exp (T) will define the exact wave function. Inclusion of doubly excited linked clusters to the wave function is termed as coupled cluster doubles wave function. Further wave function can be improved by adding the triples, quadruples and up to N-tuply excitations. The advantage is, these higher order excitations can be written as product of doubly excited configurations. For calculating amplitude using normal CC method, projection techniques are used. In terms of second quantization, T is the sum of hole-particle creation operators.

$$T = T_1 + T_2 + ... + T_N \tag{1.34}$$

Where,

$$\begin{aligned} T_1 &= \sum_{i \in occ} \sum_{a \in virt} t_i^a \left\{ a_a^\dagger a_i \right\} \\ T_2 &= \sum_{i,j \in occ} \sum_{a,b \in virt} t_{ij}^{ab} \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\} \end{aligned} \tag{1.35}$$

and is continued

The lower case letters t represents the amplitudes corresponding to the cluster operators T. The cluster amplitudes can be related to CI, provided the full expansion is considered in both the methods, however, in case of truncated CI and CC this relations does not hold true.

$$\begin{aligned} C_1 &= T_1 \\ C_2 &= T_2 + \frac{1}{2!} T_1^2 \\ C_3 &= T_3 + T_1 T_2 + \frac{1}{3!} T_1^3 \\ C_4 &= T_4 + T_1 T_3 + \frac{1}{2!} T_1^2 T_2 + \frac{1}{2!} T_2^2 + \frac{1}{4!} T_1^4 \end{aligned} \tag{1.36}$$

and the series continues.

Schrödinger equation with normal-ordered Hamiltonian can be written in the following form

$$\hat{H}_N e^T \left| \boldsymbol{\Phi}_0 \right\rangle = E_0^{corr} e^T \left| \boldsymbol{\Phi}_0 \right\rangle \tag{1.37}$$

There are various ways of solving above equation and further can be classified mainly into variational and non-variational methods that lead to various types of CC anasatz. A traditional form of CC anasatz, also known as non-variational coupled cluster (NVCC) and using this, the Schrödinger equation can be solved by applying projection technique or similarity transform method. Projection technique is implemented by projecting HF or excited configuration from left side on equation (1.37) to obtain energy or amplitude. The other method used for solving equation is similarity transform. By using similarity transformation method we obtain identical set of equations, which are obtained from projection method.

$$e^{-T}\hat{H}_N e^{T}\left|\boldsymbol{\Phi}_0\right\rangle = E_0^{corr}\left|\boldsymbol{\Phi}_0\right\rangle \tag{1.38}$$

The expansion of Hamiltonian can be done using Campbell-Baker-Hausedorff formula for $e^{-A}Be^{A}$, the Hamiltonian can be written as,

$$\tilde{H} = \hat{H}_N + [\hat{\mathrm{H}}_N, \mathrm{T}] + \frac{1}{2!}[[\hat{\mathrm{H}}_N, T], T] + ... \tag{1.39}$$

Applying Wick's theorem and the condition that the cluster operators commute within themselves result into two different terms. One set among them is represented by connected diagrams i.e. diagrams with no vertex detached from the rest and hence are termed as connected diagrams. Another set of diagrams those are termed as disconnected diagrams correspond to disconnected terms. Although the disconnected terms get cancel mutually with the terms in denominator and thus we get,

$$\mathrm{e}^{-T}\hat{H}_N e^{T} = (\hat{H}_N e^{T})_C \tag{1.40}$$

In equation (1.40) subscript C denotes the connectedness of the terms obtained from $\hat{H}_N$ and T. This connectedness confirms the size-consistency and size-extensivity. The normal order Hamiltonian $\hat{H}_N$, has two-body nature and hence it can be proved that equation (1.40) can be terminated after the quadratic power of T. The left hand side of equation (1.40) may be considered as similarity transformed Hamiltonian $\tilde{H}$.

$$\tilde{H} = e^{-T}\hat{H}_N e^{T} = (\hat{H}_N e^{T})_C \tag{1.41}$$

The resultant normal order Hamiltonian obtained after the transformation is non-Hermitian in nature and thus the resultant eigenvalues can be complex. The ground state correlation energy can be obtained as $\boldsymbol{\Phi}_0$ expectation value of $\tilde{H}$. Although the non-hermicity of CC anasatz is only valid for ground state calculations. The correlation energy can be written as,

$$E_0^{corr} = \langle \boldsymbol{\Phi}_0 | \tilde{H} | \boldsymbol{\Phi}_0 \rangle = \langle \boldsymbol{\Phi}_0 | (\hat{H}_N e^T)_C | \boldsymbol{\Phi}_0 \rangle \tag{1.42}$$

And the equation for obtaining the cluster amplitudes can be written as,

$$0 = \langle \boldsymbol{\Phi}_i^* | \tilde{H} | \boldsymbol{\Phi}_0 \rangle = \langle \boldsymbol{\Phi}_i^* | (\hat{H}_N e^T)_C | \boldsymbol{\Phi}_0 \rangle \tag{1.43}$$

A coupled set of nonlinear simultaneous equations are obtained by using equation (1.43), these equation are solved iteratively to get the cluster amplitudes [42,43-44]. At each order of iteration the a small amount of correction is added to correlation energy. On attaining self-consistency and numerical accuracy, the correlation energy using equation (1.42) can be obtained.

T amplitudes expanded up to Nth order result in to full CC form. However, the structure of CC is exponential and inclusion of non-linear terms makes the calculation complex. Hence for practical purpose one has to truncate the CC approximation. Commonly used approximation is $T = T_1 + T_2$, that is well known as coupled cluster singles and doubles (CCSD) . CC approximation, truncated at any order gives size-consistent and size-extensive results. The reason behind this is the exponential nature of wave operator, includes higher excitations through the products of $T_1 \text{and} T_2$. There can be further improvements in CC anasatz i.e. partial or full inclusion of triples CCSD(T), CCSDT [61], quadruples CCSDT(Q) and CCSDTQ, [62] etc. Thus CC theory is most accurate among all other theories.

Although NVCC method gives quite accurate results, it has its own limitation. Due to non-variational nature the energy obtained is not necessarily upper bound to ground state energy. Thus in applications like potential energy surfaces (PES), NVCC fails to converge to a right state. Also for open shell systems the NVCC does not give accurate results.

To find an alternative to the NVCC approach there are various variational methods studied in literature. The detailed discussion on them will be followed.

1.7 Stationary / Variational Coupled Cluster Approaches:

1.7.1 Expectation Value Coupled Cluster

Among the variational methods, expectation value coupled cluster (XCC) method has been studied in literature [63-67]. The series in XCC is not explicitly size-extensive or linked but can be shown that it leads to a linked functional. This was proved by Pal *et. al.* [64]. Factorizing the numerator into completely linked part and unlinked part and cancelling the unlinked part with the denominator, leads to linked term. However, this cancellation of unlinked part can be only made if the numerator as well as denominator are not truncated. We obtain a linked series as,

$$E = \left\langle \boldsymbol{\Phi}_0 \left| e^{T^\dagger} \hat{H}_N e^T \right| \boldsymbol{\Phi}_0 \right\rangle_L \tag{1.44}$$

Here in equation (1.44) the T operator is same as in NVCC i.e. hole particle creation operator while $T^\dagger$ is hole particle destruction operator. And thus $T^\dagger$ can be expanded as

$$T^\dagger = T_1^\dagger + T_2^\dagger + ... + T_N^\dagger \tag{1.45}$$

$$\begin{aligned} T_1^\dagger &= \sum_{i \in occ} \sum_{a \in virt} t_a^i \left\{ a_i^\dagger a_a \right\} \\ T_2^\dagger &= \sum_{i,j \in occ} \sum_{a,b \in virt} t_{ab}^{ij} \left\{ a_i^\dagger a_j^\dagger a_b a_a \right\} \end{aligned} \tag{1.46}$$

and so on.

Thus the cluster amplitudes are obtained by making the energy functional stationary with respect to T (or $T^\dagger$). The XCC series is non-terminating series. However, it has to be truncated for practical application. Various truncation schemes are available. Based on fixed powers of $T / T^\dagger$ truncation scheme is defined. This is symmetric truncation scheme. Pal *et. al.* [64] used this scheme in stationary determination of cluster amplitudes. However, one limitation of method was observed that fix power truncation of the functional would not give necessary upper bound results . Based on perturbation analysis, a new truncation scheme was suggested for XCC by Bartlett *et. al* [66]. In this approximation, all the terms that contribute at least at fixed order (n) in V perturbation are included. However, the method is not symmetric. The major disadvantage of XCC is, the series is non-terminating and when truncated and tested for stationarality, it leads to disconnected terms in the equation for T amplitudes as well as for derivatives. Thus the result of this is loss of size-extensivity in evaluation of properties.

1.7.2 Unitary Coupled Cluster Approach

A little different approach within variational framework called as unitary CC was proposed by Van Vleck [67] ,Primas [68] and Kutzelnigg [69]. A more symmetric truncation scheme using UCC ansatz was suggested by Bartlett [66]. UCC wavefunction makes use of anti-Hermitian cluster operator σ, which can also be written as $T - T^{\dagger}$. The cluster amplitudes can be obtained either by using variational or non-variational method. While Westhausand Mukherjee*et.al.* proposed a non-variational method for calculating cluster amplitudes [70]. Thus the energy and amplitudes can be found using UCC functional as,

$$\begin{aligned} E_0 &= \left\langle \boldsymbol{\Phi}_0 \left| e^{-\sigma} H e^{\sigma} \right| \boldsymbol{\Phi}_0 \right\rangle \\ 0 &= \left\langle \boldsymbol{\Phi}^* \left| e^{-\sigma} H e^{\sigma} \right| \boldsymbol{\Phi}_0 \right\rangle \end{aligned} \qquad (1.47)$$

Using similarity transformation, it can be written in the form of $e^{-\sigma} H e^{\sigma}$. Thus the series can be written as,

$$e^{-\sigma} H e^{\sigma} = H + [H,(T - T^{\dagger})] + \frac{1}{2!}[[H,(T - T^{\dagger})](T - T^{\dagger})] + \ldots \qquad (1.48)$$

As proposed by Kutzelnigg, the UCC can be solved variationally and the expectation value can be written as,

$$E = \frac{\left\langle \Phi_0 \left| e^{-\sigma} H e^{\sigma} \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| e^{-\sigma} e^{\sigma} \right| \Phi_0 \right\rangle} \qquad (1.49)$$

If the denominator in equation (1.49) is taken to all orders is identically equal to unity, that results into

$$E = \left\langle \Phi_0 \left| e^{-\sigma} H e^{\sigma} \right| \Phi_0 \right\rangle \qquad (1.50)$$

Thus the equation (1.50) obtained has a close relation to expectation value functional obtained by using normal CC wave operator i.e. T amplitudes.

However, there are only few studies done using UCC functional and has never been used for calculating molecular properties.

1.7.3 Extended Coupled Cluster Approach

Arponen and Bishop [71-73] suggested the bi-orthogonal functional for calculation of ground state energy using the stationary approach. The functional can be written in double-similarity transformed Hamiltonian form. An additional destruction operator is added on left hand side to the non-variational coupled cluster functional. Using double similarity transformation, the extended coupled cluster (ECC) functional can be written in the following form

$$E = \left\langle \boldsymbol{\Phi}_0 \middle| e^{\boldsymbol{\Sigma}} (He^{T})_L \middle| \boldsymbol{\Phi}_0 \right\rangle_{DL} \tag{1.51}$$

In equation (1.51),T indicates the hole-particle excitation operator while Σ indicate hole-particle destruction operator. The subscript *L* signifies linking of *T* with the Hamiltonian $\hat{H}$. This linking specifies that, it is mandatory for hole-particle operator *T* to be connected to the Hamiltonian $\hat{H}$. The *DL (double linking)* indicates the left operator Σ should either be connected to Hamiltonian $\hat{H}$ or to two different *T* operators. Thus the *DL* ensures connectedness between the terms present in equations containing Σ and *T* respectively. Functional being variational in nature, the correlation energy obtained is size-extensive. Thus the series gets naturally terminated due to the double linking of the functional. Several alternative forms of ECC have been pursued by Van Voorhis and Head-Gordon [74] and Piecuch and co-workers [75, 76]

The advantage of ECC over Non-variational CC, for calculating various molecular properties will be discussed in linear response section.

1.8 Evaluation of molecular properties through response methods

Energy derivatives have their own importance in various fields in predicting various properties like spectroscopic properties, electric, magnetic and geometric properties. There are several approaches for calculating these energy derivatives. Among them we can list the main approaches as numerical, expectation value and analytic approach. CC method, due to its ability of predicting accurate energy is also popular for calculating energy derivatives. Since the analytic approach provides most accurate results, the development of these methods has acquired a great importance in quantum mechanical methods. In this thesis we have studied electric properties as well as spectroscopic properties. Formulation and implementation of gradient i.e. first derivative of energy with respect to nuclear geometry is done.

1.8.1 Numerical Approach:

Finite field method is the very well-known and most easy approach to calculate energy derivatives. For calculation of nth order derivative we require the finite difference between the derivatives with respect to the field strength or external perturbation. There are numerous studies done using finite field approach in CC method. For instance multipole moments[7-10], dipole[7-10,77], quadrupole and higher order polarizabilities and hyperpolarizabilities[78,79] are studied in CC framework. The level of precision of the method depends on the field strength selected. Although, the method is simple most, loses its accuracy for higher order derivatives calculation. Hence one has to find an alternative for accurate property/derivative calculation.

1.8.2 Expectation Value Approach:

The analytic approach for the calculation of properties is most precise and accurate one. Expectation value approach is mostly used for calculating first order properties. The expectation value for property calculation is expressed in the following form. $\hat{O}$ is the first order property i.e. dipole operator

$$\left\langle \hat{O} \right\rangle = \frac{\left\langle \Psi \middle| \hat{O} \middle| \Psi \right\rangle}{\left\langle \Psi \middle| \Psi \right\rangle} \tag{1.52}$$

For property calculation using CC ansatz the expectation value can be written as,

$$\left\langle \hat{O} \right\rangle = \frac{\left\langle \Phi_0 \middle| e^{T^\dagger} \hat{O} e^{T} \middle| \Phi_0 \right\rangle}{\left\langle \Phi_0 \middle| e^{T^\dagger} e^{T} \middle| \Phi_0 \right\rangle} \tag{1.53}$$

In equation (1.52), Ψ is the ground state wavefunction. Numerator as well as denominator has to be expanded in order to get the expectation value of property. However, the series is non-terminating in nature and has to be truncated for practical applications. Noga and Urban [51] studied the effect of truncation on expectation value .The disadvantage with this approach is, only first order properties are accurately calculated and the higher order property calculation is tedious as well as the property calculated is not accurate. Expectation value of first order property is generally expressed as, when the Hamiltonian of the system is perturbed by an external perturbation such as electric field, the total Hamiltonian is written as sum of unperturbed Hamiltonian i.e. Hamiltonian in absence of external perturbation and perturbed Hamiltonian.

$$\hat{H} = \hat{H}_0 + \lambda\hat{O} \tag{1.54}$$

here λ represents the perturbation parameter,. Then the total energy is obtained by

$$E(\lambda) = \frac{\langle\Psi(\lambda)|H(\lambda)|\Psi(\lambda)\rangle}{\langle\Psi(\lambda)|\Psi(\lambda)\rangle} \tag{1.55}$$

To get the expectation value of energy, where λ =0,

$$\langle E^{'}\rangle = \frac{\partial E(\lambda)}{\partial\lambda}|_{\lambda=0} = \frac{\partial}{\partial\lambda}\langle\Psi(\lambda)|\hat{H}_0 + \lambda\hat{O}|\Psi(\lambda)\rangle \tag{1.56}$$

Thus partially differentiating the equation (1.55) we get,

$$\langle E^{'}\rangle = \left\langle\frac{\partial\Psi(\lambda)}{\partial\lambda}\right|H_0|\Psi\rangle|_{\lambda=0} + \langle\Psi_0|\hat{O}|\Psi_0\rangle + \langle\Psi|\hat{H}_0\left|\frac{\partial\Psi(\lambda)}{\partial\lambda}\right\rangle|_{\lambda=0} \tag{1.57}$$

Ψ_0 and $\Psi(\lambda)$ in equation (1.57) represent the unperturbed as well as perturbed wave function.

1.8.3 Analytic response Approach

Many of the properties in CC framework are calculated using analytic response approach due to the high accuracy of the method. Non-variational or fully variational methods are implemented for calculating molecular properties. Calculation of energy derivatives i.e. property, of certain order requires the amplitude derivatives along with the wave function derivatives. Thus to evaluate property using non-variational CC (NVCC) method, the derivatives of t amplitudes have to be calculated.

1.8.3.1 Analytic non-variational CC method for property calculation

The property calculation involves derivative of cluster amplitudes as well as energy derivatives and the projection technique is used for calculation of these derivatives. This projection is done from left hand side of the analytical NVCC functional. Monkhorst [80] first time applied the response approach within NVCC for evaluating properties. The NVCC wave function in presence of an external field can be expanded and $E(\lambda)$ and $T(\lambda)$ written form of Taylor series as.

$$E\left(\lambda\right) = \left\langle \Phi_0 \middle| \left(He^{T(\lambda)}\right)_C \middle| \Phi_0 \right\rangle \tag{1.58}$$

$$\begin{aligned} E(\lambda) &= E^{(0)} + \lambda E^{(1)} + \lambda^{(2)} E^{(2)} + \ldots\ldots + \lambda^{(n)} E^{(n)} \\ T(\lambda) &= T^{(0)} + \lambda T^{(1)} + \lambda^{(2)} T^{(2)} + \ldots\ldots + \lambda^{(n)} T^{(n)} \end{aligned} \tag{1.59}$$

The nth order derivative of energy with respect to field λ calculated at λ =0.

$$E^{(n)} = \frac{1}{n!} \frac{\delta^n E(\lambda)}{\delta\lambda} |_{\lambda=0} \tag{1.60}$$

Thus the derivatives of energy and amplitude derivatives in wave function derivatives can be obtained by differentiating energy as well as amplitude equation within NVCC framework. Thus using equation of NVCC energy (1.42) and amplitude equation (1.43) and taking their respective derivatives with respect to the field will provide us with the solution of derivatives of required order. It has to be underlined that the equation required for particular order contain linear derivative cluster amplitudes of the particular order and without considering the relaxation of the orbitals we can write the specific equations as,

$$E_0^{(1)} = \left\langle \Phi_0 \left| [(\hat{O}e^T)_C + (\hat{H}_N e^T T^{'})_C] \right| \Phi_0 \right\rangle \tag{1.61}$$

$$0 = \left\langle \Phi^* \left| [(\hat{O}e^T)_C + (\hat{H}_N e^T T^{'})_C] \right| \Phi_0 \right\rangle \tag{1.62}$$

With using equations (1.58) and (1.59) we obtain the first order derivatives of energy and amplitudes. Although, the method seems very simple and trivial for solving, for each mode of perturbation we need the amplitude derivatives. Thus requirement of amplitude derivatives increases the complications in the NVCC method for obtaining higher order properties.

1.8.3.2 Z-Vector Technique

This is an alternate approach to calculate the energy derivative through elimination of $t^{(1)}$ i.e. amplitude derivatives. The initial concept of Z-vector technique was proposed by Handy and Schaefer [37] who used the method for evaluating analytical derivatives for CI method. Later Bartlett and co-workers [36] introduced Z-vector technique in NVCC context based on Dalgarno's [81] interchange theorem. Thus the equations can be written in the following form

$$E_0^{corr(1)} = Y^T T^{(1)} + Q(\hat{O}) \tag{1.63}$$

$$0 = \mathrm{A}\mathrm{T}^{(1)} + B(\hat{O}) \tag{1.64}$$

$$Z^T A = Y^T \tag{1.65}$$

$$E_0^{corr(1)} = Z^T B(\hat{O}) + \mathrm{Q}(\hat{\mathrm{O}}) \tag{1.66}$$

Equation (1.63) introduces a perturbation independent vector Z^T. The $Y^T T^{(1)}$ represents the amplitude derivative while $Q(\hat{O})$ implies the Hamiltonian derivative. In equation (1.66) it is seen that the first derivative of energy is independent of wavefunction derivative. Hence there is only one set of perturbation independent amplitudes to be solved i.e. Z-vector represented in equation (1.66). However, solving the properties beyond second derivative becomes tedious and hence one has to find some other method for simplification of evaluation of property.

1.8.3.3 Constrained Variational Approach

As the name suggest and in context of the CC approach, NVCC method is made variational with the application of some constrain over it**.** Jørgensen and co-workers [38, 82, 83] introduced constrained variational approach (CVA), which extends the advantages of Z-vector technique for higher order energy derivatives. This CVA technique has been basically originated from Lagrange's undetermined multipliers method. Thus CVA approach in terms of Lagrangian can be written as follows

$$L = \langle \Phi_0 | (\hat{H}e^T)_C | \Phi_0 \rangle - \sum_{I \neq 0} \lambda_I \langle \Phi_I | (\hat{H}e^T)_C | \Phi_0 \rangle \qquad (1.67)$$

from equation (1.67), we can make a remark that first term in right hand side gives the total electronic energy of the system. $\lambda^{'}s$ are the Lagrange multipliers and are optimized with the cluster equations as the constraint. The optimization of *L* leads to equation for λ-vectors that are same as Z-vectors. Thus, in comparison with Z-vector technique CVA is computationally more feasible for higher order derivatives.

1.8.4 Property calculation using stationary approach

Stationary or variational methods have a definite advantage over NVCC method due to their nature to follow generalised Hellmann-Feynman (GHF) theorem. With (GHF) theorem we can calculate (2n+1) energy derivative with the help of nth derivative of cluster amplitudes. Bartlett and co-workers used variational i.e. stationary response approach in context of energy derivatives. Different methods were used by Jorgensen *et. al.* as well as Pal and co-workers for calculating energy derivatives using stationary response approach. Helgaker and Jorgensen proposed Lagrange multiplier technique for calculation of response functions for static perturbation. The stationary method is used and the construction of the Lagrangian is such that it will give non-variational CC equations when differentiated to λLM . Thus using this stationary technique Hellmann-Feynman Theorem can be derived. Helgaker and Jorgensen derived the time-independent Lagrange multiplier approach for evaluation of higher derivatives of energy. While

Kochet.al. [83] presented a general formalism for determining amplitudes using time-dependant method.

Pal *et. al.* developed XCC as well as UCC response approach extensively for evaluation of static properties [84] i.e. energy derivatives for molecules [85-88]. In this stationary approach the energy functional and the derivatives of the energy are represented in terms of cluster amplitudes and their derivatives. In the presence of external field the energy as well as the cluster amplitudes depend on the external perturbation. Energy and cluster amplitudes are expanded in Taylor series. Collecting powers of perturbation we get equations for various orders. To solve these equations energy functional is made stationary with respect to ground state cluster amplitudes. Pal and co-workers showed that if cluster amplitudes along with their derivatives are truncated to uniform degree, then the stationary condition $\frac{\partial E^{(i)}}{\partial T^{(i)}}=0$ gives identical set of equations for a fixed value of (i-j) [85]. For obtaining the cluster derivative of specific order, the derivative of energy functional of that order is made stationary with respect to cluster amplitudes. Thus using this Stationarity condition we can obtain the (2n+1) rule for energy derivative calculation. The major advantage of using XCC and UCC for evaluating property is, the nature of the series is non-terminating and requires truncation for practical applications. Thus the truncation of these series results in the presence of disconnected terms in calculating amplitudes as well as derivative amplitudes. This leads to loss in size-extensivity.

Thus to correct the problems present in XCC as well as UCC functional, Pal and co-workers studied another functional for property evaluation [42, 85]. It recovers all the discrepancy present in the previous two methods. Arponen and Bishop proposed the bi-orthogonal functional to calculate energy [41,71-73]. The functional contains two different set of parameters represented by bra and ket. Thus the functional can be written as

$$\begin{aligned}\left\langle \hat{H}\right\rangle &= \left\langle \Psi' \right| \hat{H} \left| \Psi \right\rangle \\ \left\langle \hat{H}\right\rangle &= \left\langle \Phi_0 \right| \left(1+\Omega\right) e^{-T} H e^{T} \left| \Phi_0 \right\rangle\end{aligned} \qquad (1.68)$$

In equation (1.68) $\left\langle \Psi' \right|$ and $\left| \Psi \right\rangle$ are the two set of parameters, those are parameterized differently. T is a hole-particle excitation operator while Ω is a linear operator and includes hole-particle de-excitation operator, the operator resembles with the T^{+} operator. Φ_0 is the Hartree-Fock determinant i.e. the reference function. Thus we can write the equations as

$$\begin{aligned} \left\langle \Psi' \middle| \Psi \right\rangle &= 1 \\ \left\langle \Phi_0 \middle| \Psi \right\rangle &= 1 \end{aligned} \tag{1.69}$$

Differentiating equation (1.68) with respect to Ω we get the NVCC equation. To obtain the fully connected theory Arponen proposed extended coupled cluster theory (ECC). After the double similarity transform, the functional can be written as,

$$\begin{aligned} \left\langle E \right\rangle &= \left\langle \Phi_0 \middle| e^{\Sigma} e^{-T} H e^{T} e^{-\Sigma} \middle| \Phi_0 \right\rangle_{DL} \\ \left\langle E \right\rangle &= \left\langle \Phi_0 \middle| e^{\Sigma} (H e^{T})_L \middle| \Phi_0 \right\rangle_{DL} \end{aligned} \tag{1.70}$$

We can correlate between the equation (1.69) and (1.70) as $\left\langle \Psi' \right| = \left\langle \Phi_0 \right| e^{\Sigma} e^{-T}$ and $\left| \Psi \right\rangle = \Sigma\ e^{T} e^{-\Sigma} \left| \Phi_0 \right\rangle$. The subscript *L* represents the direct linking of *T*-amplitudes with the Hamiltonian *H*. The subscript *DL* indicates the double linking of the functional i.e. the left operator Σ either has to be connected to Hamiltonian *H* or should be connected to at least two different *T* amplitudes. The double linking ensures the connectedness in the energy as well as amplitude terms. Also the energy derivatives along with the cluster amplitude derivatives are connected at any order of truncation.

The hole-particle creation T and destruction Σ amplitudes can be written in e second quantised form as

$$\begin{aligned} T &= T_1 + T_2 + T_3 + ... + T_N \\ T_1 &= \sum_{i,a} t_i^a \{a_a^{\dagger} a_i\} \\ T_2 &= \sum_{i,j,a,b} t_{ij}^{ab} \{a_a^{\dagger} a_b^{\dagger} a_j a_i\} \end{aligned} \tag{1.71}$$

$$\begin{aligned}&\Sigma = \Sigma_1 + \Sigma_2 + \Sigma_3 + ... + \Sigma_N \\ &\Sigma_1 = \sum_{i,a} \sigma_a^i \{a_i^\dagger a_a\} \\ &\Sigma_2 = \sum_{i,j,a,b} \sigma_{ab}^{ij} \{a_i^\dagger a_j^\dagger a_b a_a\}\end{aligned} \tag{1.72}$$

Advantage with the ECC anasatz is the series expanded gets naturally terminated. Though the series is naturally terminating, the truncation happens at higher order. Thus for practical applications we need to use some truncation scheme. For example, for singles and doubles approximation, the term with maximum number of Σ and T amplitude terms is $\Sigma_1^6 V T_2^4$, it means the total power $(\Sigma + T)$ is 10 while that with the perturbative order is 17 for this term. However, such higher order terms do not improve the correlation energy to any noticeable order. The calculation of such higher order terms is computationally very expensive and hence the series is truncated at low order for practical applications. Quadratic truncation of left as well as right cluster amplitudes using Bruckner orbitals and elimination of singles terms was proposed by Head-Gordon *et. al.* [74]. This truncation scheme was found accurate for calculation of energy of different systems.

To calculate the ground state cluster amplitudes for T and Σ variationally, energy is made stationary with respect to t and σ .

$$\frac{\partial E^{(i)}}{\partial \sigma^{(0)}} = 0; i = 0,1,..... \tag{1.73}$$

$$\frac{\partial E^{(i)}}{\partial t^{(0)}} = 0; i = 0,1,.... \tag{1.74}$$

solving equations (1.73) and (1.74), we obtain equations for t and σ respectively. Thus being variational method, the Hellman-Feynman theorem i.e. (2n+1) holds good, for evaluating the energy derivatives.

$$\begin{aligned}&E^{(1)} = \langle \Phi_0 | e^{\Sigma} (H^{(1)} e^T)_L | \Phi_0 \rangle_{DL} + \\ &\langle \Phi_0 | e^{\Sigma} (\Sigma^{(1)} H e^T)_L | \Phi_0 \rangle_{DL} + \langle \Phi_0 | e^{\Sigma} (H e^T T^{(1)})_L | \Phi_0 \rangle_{DL}\end{aligned} \tag{1.75}$$

For calculating higher order derivatives of energy i.e. higher order response properties, we require the derivatives of t and σ amplitudes. For instance if we have to calculate the second order derivative of energy then we require first order derivative of t and σ amplitudes.

Similarly higher order derivatives using Hellman-Feynman theorem can be obtained with these derivatives. The L (*linked*) and DL (*Double linked*) have the same meaning as signified in equation (1.70). Therefore, the ECC functional not only gives the connected diagrams and terms for energy, but also gives connectedness in energy derivative terms as well. General equation to obtain the amplitudes $\boldsymbol{\Sigma}^{(1)}$ and $t^{(1)}$ are given by equation (1.76) and (1.77),

$$\frac{\partial E^{(1)}}{\partial \sigma^{(0)}} = 0 \tag{1.76}$$

$$\frac{\partial E^{(1)}}{\partial t^{(0)}} = 0 \tag{1.77}$$

$$\begin{aligned}&\left\langle \boldsymbol{\Phi}_{ij}^{ab} \right| \hat{V} + \hat{V}t_1^{(0)} + (\hat{F} + \hat{V})t_2^{(0)} + \frac{1}{2!}\hat{V}t_1^{(0)}t_1^{(0)} + \hat{V}t^{\,(0)}{}_1 t_2^{(0)} + \frac{1}{2!}\hat{V}t_2^{(0)}t_2^{(0)} + \boldsymbol{\Sigma}_1^{(0)}\hat{V}t_2^{(0)} + \\ &\hat{V}t_2^{(0)}(t_1^{(0)})^2 + \frac{1}{3!}\hat{V}(t_1^{(0)})^3 + \frac{1}{4!}\hat{V}(t_1^{(0)})^4 \left| \boldsymbol{\Phi}_0 \right\rangle = 0\end{aligned} \tag{1.78}$$

$$\begin{aligned}&\left\langle \boldsymbol{\Phi}_{i}^{a} \right| \boldsymbol{\Sigma}_1^{(0)}\hat{V} + (\hat{F} + \hat{V})t_1^{(0)} + \hat{V}t_2^{(0)} + Vt^{\,(0)}{}_1 t_2^{(0)} + \frac{1}{2!}\hat{V}t_1^{(0)}t_1^{(0)} + \boldsymbol{\Sigma}_1^{(0)}\hat{V}t_2^{(0)} + \\ &+\boldsymbol{\Sigma}_1^{(0)}\hat{V}t_1^{(0)} + \boldsymbol{\Sigma}_2^{(0)}\hat{V}t_2^{(0)} + \hat{V}t_2^{(0)}(t_1^{(0)})^2 + \frac{1}{3!}\hat{V}(t_1^{(0)})^3 \left| \boldsymbol{\Phi}_0 \right\rangle = 0\end{aligned} \tag{1.79}$$

Equations (1.78) and (1.79) give us the derivatives of cluster amplitudes $t_2^{(1)}$ and $t_1^{(1)}$ and in similar way equations for $\boldsymbol{\Sigma}_2^{(0)}$ and $\boldsymbol{\Sigma}_1^{(0)}$ amplitudes are given as

$$\begin{aligned}&\left\langle \boldsymbol{\Phi}_0 \right| \hat{V} + \boldsymbol{\Sigma}_1^{(0)}\hat{V} + \boldsymbol{\Sigma}_2^{(0)}(\hat{F} + \hat{V}) + \frac{1}{2!}\boldsymbol{\Sigma}_1^{(0)}\boldsymbol{\Sigma}_1^{(0)}\hat{V} + \boldsymbol{\Sigma}_1^{(0)}\boldsymbol{\Sigma}_2^{(0)}\hat{V} \\ &+\boldsymbol{\Sigma}_1^{(0)}\hat{V}t_1^{(0)} + \boldsymbol{\Sigma}_2^{(0)}\hat{V}t_1^{(0)} + \boldsymbol{\Sigma}_2^{(0)}(\boldsymbol{\Sigma}_1^{(0)})^2\hat{V} + \boldsymbol{\Sigma}_2^{(0)}\hat{V}t_2^{(0)} + \frac{1}{3!}(\tilde{\boldsymbol{\Sigma}}_1^{(0)})^3\hat{V} + \frac{1}{4!}(\boldsymbol{\Sigma}_1^{(0)})^4\hat{V} \left| \boldsymbol{\Phi}_{ij}^{ab} \right\rangle = 0\end{aligned} \tag{1.80}$$

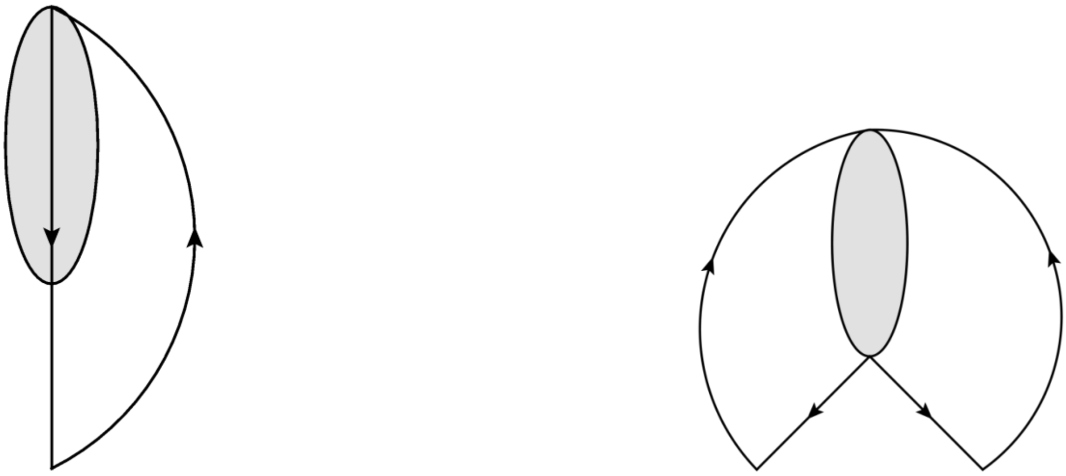
$$\begin{aligned}&\left\langle \boldsymbol{\Phi}_0 \middle| \hat{V}t_1^{(0)} + \boldsymbol{\Sigma}_1^{(0)}(\hat{F}+\hat{V}) + \boldsymbol{\Sigma}_2^{(0)}\hat{V} + \boldsymbol{\Sigma}_1^{(0)}\hat{V}t_1^{(0)} + \boldsymbol{\Sigma}_1^{(0)}\hat{V}t_2^{(0)} \right.\\ &+\boldsymbol{\Sigma}_2^{(0)}\hat{V}t_1^{(0)} + \boldsymbol{\Sigma}_2^{(0)}\hat{V}t_2^{(0)}t_1^{(0)} + \boldsymbol{\Sigma}_2^{(0)}\hat{V}t_2^{(0)} + \frac{1}{2!}\boldsymbol{\Sigma}_1^{(0)}\boldsymbol{\Sigma}_1^{(0)}\hat{V} + \\ &\left. \boldsymbol{\Sigma}_2^{(0)}\hat{V}t_2^{(0)}t_1^{(0)} + \frac{1}{2!}\boldsymbol{\Sigma}_2^{(0)}\hat{V}(t_1^{(0)})^2 + \frac{1}{3!}\boldsymbol{\Sigma}_2^{(0)}\hat{V}(t_1^{(0)})^3 \middle| \boldsymbol{\Phi}_i^a \right\rangle = 0\end{aligned} \tag{1.81}$$

Thus stationary equation for $E^{(1)}$ can be given as,

$$\begin{aligned}E_{Stat}^{(1)} &= \left\langle \Phi_0 \middle| \hat{O}t_1^{(0)} + \Sigma_1^{(0)}\hat{O}t_1^{(0)} + \Sigma_2^{(0)}\hat{O}t_2^{(0)} \right.\\ &\left. + \frac{1}{2!}\Sigma_1^{(0)}\hat{O}t_1^{(0)}t_1^{(0)} + \Sigma_2^{(0)}\hat{O}t_1^{(0)}t_2^{(0)} \middle| \Phi_0 \right\rangle\end{aligned} \tag{1.82}$$

With these cluster amplitudes derivatives and application of Hellman-Feynman theorem we can find the derivative up to third order i.e. till first hyperpolarizability.

Solving the algebraic equation for calculating energy as well as energy derivatives becomes tedious and hence the diagrammatic techniques are used to simplify the equations.



S2VT1

S2VT1T

Digram 1: Closed connected diagrams to calculate correlation energy.

S2V

S2VT1

Diagram: 2 Open connected diagrams for amplitude

The property calculations using ECC functional within coupled cluster singles and doubles (CCSD) approach has been studied by Pal and co-workers [42-44]. For this study they have truncated the ECC functional up to cubic order i.e. total number of amplitudes is of cubic order. This ECCSD method has been extensively used to study electric properties such as dipole moment, polarizability, first hyperpolarizability of different systems and these are studied at equilibrium geometry [42, 88]. The single bond stretching has also been studied [90]. Along with these property studies, a fairly difficult magnetic property calculation has also been perceived by Pal and co-workers [43-44]. Diamagnetic and Paramagnetic magnetizabilities of small molecules have been calculated using ECCSD approximation. Nuclear magnetic shielding, which is responsible for prediction of presence of nuclei is also calculated using ECC approach and is reported by Vaval and co-workers [91].

1.9 Electric Properties:

Dipole moment, Dipole Polarizability, Quadrupole moment, Dipole-Quadrupole polarizability and various electric properties are basically energy derivatives with respect to electric field. These properties are useful in determining structure and different characteristics of molecular system. Analytical evaluation of these properties becomes important because of limitations to experimental techniques. Electric field acts as a perturbation and interacts with the charged particles i.e. electrons and thus adds scalar potential to the Hamiltonian. Thus the dipole moment and dipole polarizability are first and second derivative of energy with respect to electric field, while quadrupole moment is first derivative of energy with respect to field gradient while dipole-quadruple polarizability is second derivative of energy with respect to field and field gradient. Thus the energy in presence of electric field is written as,

$$E = E_0 + \lambda \frac{\partial E}{\partial \lambda} + \frac{\lambda^2}{2!} \frac{\partial^2 E}{\partial \lambda^2} + \dots. \quad (1.83)$$

$$E = E_0 + \mu.\lambda + \alpha.\lambda^2 + \dots \quad (1.84)$$

λ is the perturbation parameter. In this equation the energy is expanded in terms of perturbation i.e. with respect to electric field. The E_0 is unperturbed energy while $\frac{\partial E}{\partial \lambda}$ is the first order change in energy i.e. dipole moment μ. Second order change is presented by polarizability α that is $\frac{\partial^2 E}{\partial \lambda^2}$ in equation (1.83). All the calculations are done at field equal to 0.

$$\mu = \left(\frac{\partial E}{\partial \lambda} \right)_{\lambda=0} \quad (1.85)$$

$$\alpha = \left(\frac{\partial^2 E}{\partial \lambda^2} \right)_{\lambda=0} \quad (1.86)$$

The dipole moment and polarizability calculation are presented by equation (1.85) and (1.86). The electric property calculation is important for designing of non-linear optical materials. The quadrupole moment is experimentally difficult to observe while this property can be calculated by *ab-initio* methods. Calculation of quadrupole moments is essential for predicting higher order properties like dipole-quadrupole polarizability. Dipole-quadrupole polarizability is important for Raman scattering studies as well as for light scattering induced spectra [12, 13].

$$\Theta_{ij} = \frac{\partial E}{\partial \lambda_{ij}} \tag{1.87}$$

$$A_{i,jk} = \left(\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_{jk}} \right)_{\lambda=0} \tag{1.88}$$

Equations (1.87) and (1.88) give the expression for quadrupole moment and dipole-quadrupole polarizability. Gradients of dipole-quadrupole polarizability are important for the prediction of Vibrational Raman Optical Activity (VROA) intensities [12, 13].

1.10 Spectroscopic Properties

Infrared intensities (IR) [92-95], Raman intensities and Vibrational frequencies are important spectroscopic properties to predict the molecular structure and physical properties related to the molecule. IR intensity is mixed derivative i.e. derivative of dipole moment with respect to nuclear co-ordinate i.e. with respect to geometry and Raman intensity is the mixed derivative i.e. derivative of polarizability with respect to geometry. Vibrational frequency is second derivative of energy with respect to nuclear geometry. The theoretical prediction of the IR spectroscopic constants is well documented. Studies on IR spectra calculation are available in the literature for a wide variety of methods, starting from semi-emphirical, Hartree–Fock (HF) [95 -98], Moller–Plesset perturbation theory (MP2) [99] to highly accurate SRCC methods[100]. Basis set dependence and effect of electron correlation on IR spectroscopic property are also studied [92, 95]. Recently, Helgaker and co-workers [101] have studied harmonic vibrational frequencies using coupled cluster connected quadruples and quintuples. *Ab initio* study of Raman spectroscopic properties is less abundant because of obvious difficulties in the evaluation of mixed third order derivative of energy. There are only a few studies at the Hartree–Fock [102, 103] and MP2 level [104]. At the CC level of theory, Raman scattering cross section has been studied[105,106] . Raman intensities for small molecules using analytic CCSD method have been reported by Neill et al.[107]. Analytically IR and Raman intensities can be calculated using gradient of dipole moment and polarizability while vibrational frequency is calculated using the Hessian.

$$\begin{aligned} \frac{d\mu_i}{dR_K} &= -\frac{d^2E}{dR_K dF_i} \\ \frac{d\alpha_{ij}}{dR_K} &= -\frac{d^3E}{dR_K dF_i dF_j} \end{aligned} \tag{1.89}$$

Thus equation (1.89) gives the IR and Raman intensity.

1.10.1 Details of the theory used for the calculation of IR and Raman spectroscopic properties:

The theory for obtaining the spectroscopic properties is given in detail. In the harmonic approximation, the vibrational eigen modes of a given system can be found by solving the eigenvalue problem

$$\sum_{k=1}^{3N}(H_{jk} - \lambda M_{jk}) = 0, j = 1...3N, \lambda_i = (2\pi\nu_i) \tag{1.90}$$

$$\sum_{k=1}^{3N}\sum_{l=1}^{3N} X_{ki}M_{kl}X_{lj} = \delta_{ij} \tag{1.91}$$

$$M_{kl} = \delta_{kl}m_n \tag{1.92}$$

In Eq. (1.90), N is the number of atoms, H is the hessian matrix of the system, X_{ki} are the elements of the ith eigenvector, m_n is the mass of the nth atom and ν_i is the frequency of the

i^{th} mode. A displacement U_{ki} in the direction of the i^{th} eigenvector can then be written as

$$U_{ki} = Q_i X_{ki} \tag{1.93}$$

Where Qi is referred as a normal-mode co-ordinate. Often, the derivatives of some physical property A with respect to Qi are required. If the derivatives of A are already known with respect to the external (Cartesian) atomic coordinates R_k, the required expression can easily be obtained from the following equation

$$\frac{dA}{dQ_i} = \sum_{k=1}^{3N} \frac{\partial A}{\partial R_k} X_{ki} \tag{1.94}$$

The first-order infrared intensity of the i^{th} mode is given by

$$I_i^{IR} = \frac{N\pi}{3c} \left| \frac{d\mu}{dQ_i} \right|^2 \tag{1.95}$$

Where N is the particle density, c is the velocity of light and μ is the electric dipole moment of the system.

Evaluation of Raman-scattering intensity is slightly more complicated. The static Raman intensity for ith eigen mode is given by

$$I_i^{Raman} = 45\left(\frac{d\alpha}{dQ_i}\right)^2 + 7\left(\frac{d\beta}{dQ_i}\right)^2 = 45\alpha'^2 + 7\beta'^2 \tag{1.96}$$

Where

$$\alpha' = \frac{1}{3}(\tilde{\alpha}_{xx}' + \tilde{\alpha}_{yy}' + \tilde{\alpha}_{zz}') \tag{1.97}$$

$$\beta^{'2} = \frac{1}{2}[(\tilde{\alpha}_{xx}^{'2} - \tilde{\alpha}_{yy}^{'2}) + (\tilde{\alpha}_{xx}^{'2} - \tilde{\alpha}_{yy}^{'2}) + (\tilde{\alpha}_{yy}^{'2} - \tilde{\alpha}_{zz}^{'2})]$$
$$+3[(\tilde{\alpha}_{xy}^{'2} + \tilde{\alpha}_{yz}^{'2} + \tilde{\alpha}_{xz}^{'2})] \tag{1.98}$$

And is given by

$$\rho_i = \frac{3\beta^{'2}}{45\alpha^{'2} + 4\beta^{'2}} \tag{1.99}$$

A depolarization ratio describes the ratio of the intensities perpendicular and parallel to the incident polarization. In the above equations, α’ is the mean polarizability derivative, β’ is the anisotropy of polarizability tensor derivative and I_i^{Raman} is the Raman scattering activity of ith mode. Prime denotes derivative with respect to the normal co-ordinate Q. These formulas are derived within the double harmonic approximation, which means that higher-order changes of the energy, dipole moment, and polarizability with respect to the normal-mode co-ordinate are neglected. Calculation of IR and Raman intensities along with vibrational frequencies for small molecules has been carried out using ECC approach. The details of calculations are discussed in chapter 2.

1.11 Geometric Derivatives

The calculations of reaction pathways as well as many properties depend upon the geometry of molecule. Many of the spectroscopic properties like IR, Raman intensities, vibrational frequencies can be predicted more precisely with the geometric derivatives. The first order derivative of energy with respect to nuclear co-ordinate or geometry is called as gradient whereas the second derivative of energy with respect to nuclear co-ordinates is called as hessian. Thus the wave function response is required for these derivatives and wave function changes at each order of geometric perturbation. To calculate the wave function response the Coupled Perturbed Hartree-Fock equations are solved and therein the derivative coefficients are obtained. Thus the standard HF equation in unperturbed form can be written as,

$$F^{(0)}C^{(0)} = S^{(0)}C^{(0)}\varepsilon^{(0)} \tag{1.100}$$

The superscript (0) refers to unperturbed system. In presence of perturbation the equation becomes,

$$F^{(1)}C^{(0)} + F^{(0)}C^{(1)} = S^{(1)}C^{(0)}\varepsilon^{(0)} + S^{(0)}C^{(1)}\varepsilon^{(0)} + S^{(0)}C^{(0)}\varepsilon^{(1)} \tag{1.101}$$

Where Fock matrix (F), overlap matrix (S), coefficient matrix (C) and orbital energy matrix (ε) are expanded in terms of perturbation parameters. Thus we obtain first order CPHF equations by collecting the perturbed terms together.

$$(F^{(0)} + S^{(0)}\varepsilon^{(0)})C^{(1)} = (F^{(1)} + S^{(1)}\varepsilon^{(0)} + S^{(0)}\varepsilon^{(1)})C^{(0)} \tag{1.102}$$

Thus equations (1.101) and (1.102) give the perturbed MO coefficients in terms of unperturbed quantities.

Using orthonormality condition of molecular orbitals $C^{\dagger(0)}S^{(0)}C^{(0)} = 1$, the equation becomes,

$$C^{\dagger(1)}S^{(0)}C^{(0)} + C^{\dagger(0)}S^{(1)}C^{(0)} + C^{\dagger(0)}S^{(0)}C^{(1)} = 0 \tag{1.103}$$

Thus $F^{(1)}$ term is given as,

$$F^{(1)} = h^{(1)} + G^{(1)}D^{(0)} + G^{(0)}D^{(1)} \tag{1.104}$$

Here in equation (1.104) $h^{(1)}$ represents the one-electron (core) matrix, D is the density matrix, G is the tensor containing two electron integrals. The density matrix can be written as a product of MO coefficients

$$\begin{aligned} D^{(0)} &= C^{\dagger(0)}C^{(0)} \\ D^{(1)} &= C^{\dagger(1)}C^{(0)} + C^{\dagger(0)}C^{(1)} \end{aligned} \tag{1.105}$$

The quantities $S^{(1)}$, $h^{(1)}$ and $g^{(1)}$ are first derivatives of overlap matrix, one and two electron integrals.

When the perturbation is introduced, the stationary condition means that there is change in the molecular orbitals i.e. mixing of unperturbed MOs. Thus unitary transformation can show the change in MO.

$$C^{(1)} = U^{(1)} C^{(0)} \tag{1.106}$$

Simplifying equation (1.102) by substituting $C^{\dagger^{(0)}} S^{(0)} C^{(0)} = 1$ and $C^{\dagger^{(0)}} F^{(0)} C^{(0)} = E$ we get the CPHF equation in matrix form.

$$EU^{(1)} - U^{(1)} E = C^{\dagger^{(0)}} S^{(1)} C^{(0)} E - C^{\dagger^{(0)}} F^{(1)} C^{(0)} + E^{(1)} \tag{1.107}$$

The CPHF equations are generally linear and can be solved with standard matrix operations. These equations are solved in iterative manner. The size of U matrix is number of occupied orbitals times number of virtual orbitals. The formulation of CPHF equations can be done either in molecular orbital (MO) basis or atomic orbital (AO) basis. Computationally MO basis is advantageous to use but the integrals are available in AO basis. Hence AO's are used in most of the cases. For each perturbation one CPHF equation is solved. There are 3components (F_x, F_y, F_z) for electric as well as for magnetic field. For geometry perturbation there will be 3N-6 co-ordinates where N is number of atoms.

For calculation of higher order derivatives CPHF procedure can be generalized. If we extend the expansion to second-order, it allows derivation of an equation for the second-order change in the MO coefficients, by solving a second-order CPHF equation etc. First time the calculation of analytic gradient was done by Pulay in context of HF energy [108,109].

1.12 Static Correlation and Multi-reference Methods.

Single reference methods treat closed shell systems with single dominating determinant in proper way. This single reference determinant is also called as reference configuration. The closed shell systems as well as some open shell systems are described by the single dominant determinant. The electron correlation arising in due to weak interactions between different reference configurations is known as dynamical correlation. Apart from the dynamic correlation, there exists static correlation which dominates when many of the determinants along with reference configuration become equally important. This is popularly known as multi reference (MR) state. Many of the chemical systems have degenerate or quasi-degenerate states for e.g. open shell systems, potential energy surfaces, and excited states of molecules. SRCC or NVCC cannot describe such systems and hence one has to look for more advanced theories like MR. Alike single reference methods, there are various MR methods available in the literature. Some of them can be articulated depending upon their accuracy to predict the electron correlation. Multi-reference Self consistent field (MCSCF) [110], Multi-reference configuration interaction (MRCI)[111-114], Multi-reference Perturbation Theory (MRPT) [115,116] ,Multi-reference coupled cluster methods (MRCC)[117-122]. Among all these methods MRCC methods are the most precise and accurate once for predicting properties. In MRCC approach Fock-Space multi-reference coupled cluster (FSMRCC) methods are the popular once for property calculations.

Objective and Scope of the thesis:

The focus of the thesis is on molecular property evaluation using ECC method. Apart from electric properties, properties which are mixed derivatives like IR, Raman intensities are calculated. Vibrational frequencies, which are derivatives of energy with respect to geometry, are calculated for small molecules. We have implemented non-iterative triples correction in ECC method for calculation of IR, Raman intensities as well as for vibrational frequencies. We have used semi-numerical approach in our calculations except for vibrational frequencies, which are calculated using numerical approach. These results are reported in chapter 2. Implementation of ECCSD method for calculation of quadrupole moments, dipole quadrupole polarizability of small molecules is done. Here we have compared the cubic-ECCSD with ECCSD in which the T amplitudes are taken up to all orders of T i.e. t_1^4 , while the left amplitude are truncated at quadratic order. The current approximation gives better results than previous one and for tetrafluoromethane the results are in good agreement with the experimental results. The potential energy surface using decoupled approach within ECC method has been studied and compared with coupled ECC, NVCC methods. The comparative study shows that the decoupled approach shows better convergence compared to all other methods with reference to FCI method where ever available. Formulation and implementation of analytical gradient within ECC method has done in chapter 4. With the analytical gradient i.e. first order derivative of energy with respect to geometry we can accurately calculate IR, Raman intensities, chemical reaction pathways and many more molecular properties. Chapter 6 gives the insights of future scope and summary of thesis work.

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Chapter 2

Extended coupled cluster for Raman and infrared spectra of small molecules

In this chapter we study the harmonic vibrational frequencies, infrared (IR) intensities, Raman intensities and depolarization ratio using extended coupled cluster method. Raman and IR intensities are mixed derivatives of energy with respect to the electric field and geometric perturbation whereas vibrational frequencies are derivatives of energy with respect to geometry. We use semi-numerical approach to obtain these derivatives. We have studied the effect of electron correlation and basis set for the above properties. We compare our results with non-variational coupled cluster and experimental values, wherever available. We have studied HF, BH, CH^+, CO and H_2CO molecules in different basis sets. For HF molecule, benchmarking is done with full CI values and basis set convergence is studied for this molecule. Effect of triples is studied for all the molecules.

2.1 Introduction

There is interest in the accurate calculation of vibrational non-linear optical properties due to their importance in the prediction of molecular structure. There are several studies on the incorporation of electron correlation for the prediction of IR [1–3] and Raman spectroscopic properties. IR and Raman intensities are derivatives of dipole moment/ polarizability with respect to the geometry respectively. Molecular properties are sensitive to electron correlation and basis set. Single reference coupled cluster (SRCC) method [4–7], even in its approximate form, has emerged as a state of the art method due to its infinite partial summation of the important terms and size-extensivity, for the calculation of energy and energy derivatives of closed shell molecules. SRCC method has also been extensively used for the accurate calculation of molecular properties [8,9], gradients [10,11], geometry optimization and potential energy surfaces [12,13] at equilibrium or near-equilibrium geometry. First order properties are obtained using the expectation value method. However, for higher order properties it is desirable to have a closed analytic method for evaluation of energy derivatives.

Coupled cluster (CC) response formulation in the single reference context has been extensively studied. Conventionally, the Z-vector technique was first used by Handy and Schaefer [14] in the context of configuration interaction (CI). This was later ex-tended by Bartlett and co-workers [15] for the SRCC response approach. This made the SRCC method practicable for gradient calculations. However, the extension of such a procedure to higher order properties is quite complex. On the other hand, Lagrange multiplier based approach, introduced by Jørgensen and coworkers [16], which is identical to the Z-vector method for first order properties can easily be extended to higher order properties due to the explicit stationary nature. While Lagrange multiplier method is based on constrained variation method, the explicit variation of an appropriate functional without any constraint has also been used. The more popular of such functionals is expectation value approach (XCC). This functional was used by Pal and co-workers, [17– 19] perturbatively correct (XCC-n) was used by Bartlett and co-workers [20]. Unitary CC (UCC) [21] and extended coupled cluster (ECC) [22, 23] are some of the functionals in the literature. Among these functionals, XCC and ECC have been seriously studied for energy and properties. XCC, even in the finite many body truncation of the cluster operator, is non-terminating. ECC functional, however, has two sets of parameters one for the left and the other for right vectors and can be reformulated to have a double linked structure. Double linking ensures natural termination of the series as well as the connectedness of the cluster amplitudes and amplitude derivatives. The resultant energy and energy derivatives, thus, remain size-extensive. For the above reasons, ECC has turned out to be an attractive choice for the calculation of response properties. Though the ECC functional is naturally terminating, the exact termination occurs at quite a high order. Hence, for all practical purposes one needs to device a physically motivated truncation scheme. Pal and co-workers have used ECC functional extensively for the electric properties [24, 17, 25] as well as for magnetic properties [26, 27] using a scheme which includes total power in cubic T and Σ amplitudes within the singles and doubles approximation (ECCSD). Several alternative forms of ECC have been pursued by Van Voorhis and Head-Gordon [28] and Piecuch and co-workers [29, 30]. In this chapter we have used ECCSD functional with full (He^T) approximation and quadratic approximation of left exponential. Further, inclusion of partial triples in a non-iterative manner is implemented for all the molecules.

The theoretical prediction of the IR spectroscopic constants is well documented. Studies on IR spectra calculation are available in the literature for a wide variety of methods, starting from semi-emphirical, Hartree–Fock (HF) [31–34], Moller–Plesset perturbation theory (MP2) [35] to highly accurate SRCC methods [10]. Basis set dependence and effect of electron correlation on IR spectroscopic property are also studied [3,1]. Recently, Helgaker and co-workers [36] have studied harmonic vibrational frequencies using coupled cluster connected quadruples and quintuples. It is documented [36] that the inclusion of full triples i.e. CCSDT offers no improvement to the harmonic frequencies compared to the inclusion of partial triples CCSD (T). *Ab initio* study of Raman spectroscopic properties is less abundant because of obvious difficulties in the evaluation of mixed third order derivative of energy. There are only a few studies at the Hartree–Fock [37,38] and MP2 level [39]. At the CC level of theory, Raman scattering cross section has been studied [40, 41]. Raman intensities for small molecules using analytic CCSD method have been reported by Neill et al. [42].

Up to now, all the studies on IR and Raman spectroscopic properties have been carried out using traditional non-variational SRCC. ECC, being variational, is appropriate for the higher order properties. The objective of the present chapter is to implement and test the semi-numerical approach for the calculation of IR and Q branch Raman spectroscopic properties using ECCSD functional and to study the effect of partial triples for carbon monoxide and formaldehyde where effect of correlation might be crucial. The chapter is organized as follows. Section 2.2 gives a brief theory of the ECC method and computational details of calculation of spectroscopic constants. Results and discussion on them are described in Section 2.3. Section 2.4 contains conclusions.

2. 2 Theory

The bi-orthogonal coupled cluster functional was proposed by Arponen and Bishop [22, 23]. The functional is also known as ECC functional and contains a significant extension of the standard SRCC functional. It uses a bi-orthogonal set of parameters for the left and right vectors. The functional is given by

$$E = \langle H \rangle = \langle \Phi_0 | e^{\Sigma} (He^{T})_L | \Phi_0 \rangle_{DL} \tag{2.1}$$

Here subscript L denotes that the T operator to the right of the Hamiltonian H is linked to H, subscript DL (double linking) implies that the left operator Σ is either connected to the Hamiltonian H or to two different T operators. The double linking ensures that the series is naturally terminating. The cluster amplitudes are obtained using following equations.

$$\frac{\delta E}{\delta t^{(0)}} = 0; \frac{\delta E}{\delta \sigma^{(0)}} = 0 \tag{2.2}$$

where $t^{(0)}$ and $\sigma^{(0)}$ are amplitudes for T and Σ operators respectively. The double linking also ensures that the stationary equations resulting from the variation of the ECC functional with respect to the cluster amplitude are connected. Hence energy and properties are size-extensive. Since the formulation is stationary, the dipole moment can be obtained by Hellmann–Feynman theorem using only the stationary values of cluster amplitudes. An explicit derivative of energy functional with respect to electric field, $E^{(1)}$ is obtained by replacing either the Hamiltonian by derivative Hamiltonian i.e. dipole operator in this case or one of the cluster operators by the derivative of the cluster operators

$$E^{(1)} = \langle \Phi_0 | e^{\Sigma} (He^T)_L | \Phi_0 \rangle_{DL} + \langle \Phi_0 | e^{\Sigma} [\Sigma^{(1)} (He^T)_L + (He^T T^{(1)})_L] | \Phi_0 \rangle_{DL} \tag{2.3}$$

In Eq. (2.3) the T and its derivative T $^{(1)}$, are connected to the Hamiltonian derivative or to the Hamiltonian (as the case may be) and similarly the Σ or its derivative $\Sigma^{(1)}$, will either be connected to the Hamiltonian derivative or to the Hamiltonian (as the case may be) or to two different T operators. Stationarity of this explicit derivative functional E $^{(1)}$ with respect to the amplitudes of Σ and T operators provides us with the first order response amplitudes. Thus, the first derivative amplitudes of Σ and T operators are obtained as solutions of the following set of equations.

$$\frac{\delta E^{(1)}}{\delta t^{(0)}} = 0; \frac{\delta E^{(1)}}{\delta \sigma^{(0)}} = 0 \tag{2.4}$$

Eq. (2.4) provides us with the equation for $\sigma^{(1)}$ and $t^{(1)}$ amplitudes. The double-linked structure of the $E^{(1)}$ leads to the connectivity of the derivative cluster amplitudes. Thus, the resulting higher order properties (up to first hyper-polarizability) are size-extensive [25]. It is easy to observe that the linearized approximation of the left exponential leads to the T amplitudes, which are same as the SRCC amplitudes. In such a case, the left amplitudes are the standard K vector or Z-vector amplitudes of the SRCC response [15, 16]. However, ECC is significantly different from the SRCC. In ECC, the left exponential introduces several higher order terms. In this chapter, we have retained the full form of $\left(He^T\right)_C$ in singles and doubles approximations and truncated the left exponential up to quadratic. Thus this introduces additional set of terms $\left\langle \phi_0 \left| \Sigma^2 \left(He^T\right)_L \right| \phi_0 \right\rangle_{DL}$ compared to the SRCC. These terms are capable of introducing higher order corrections necessary, in particular, for bond stretch [9, 28]. With the above approximation, Equations. (2.2) and (2.4) are solved initially in singles and doubles approximation for T and Σ.

To study the effect of triples, we have implemented partial triples (ECCSD (T)) in a non-iterative manner. The scheme of inclusion of triples is as follows. First with the CCSD amplitudes, we construct the left and right triples amplitudes i.e. σ_3 and t_3 amplitudes by including VT_2 and $\Sigma_2 V$ respectively in the triples equation, where V denotes the two particle operator. Then we take the effect of triples amplitudes in the doubles equation through VT_3 terms in σ_2 amplitude equation and $\Sigma_3 V$ terms in the t_2 amplitude equation. $\Sigma_3 \mu T_3$ enters in the energy derivative/dipole moment. Since σ_3 and t_3 amplitudes are of minimum second order in perturbation, the dipole moment is correct at least up to the fourth order due to triples. A similar procedure is followed for derivative amplitude equations.

Based on the definition of dipole moment and polarizability, we have calculated the derivatives of these properties with respect to the atomic co-ordinates using a semi-numerical scheme.

$$\begin{aligned} \frac{d\mu_i}{dR_K} &= -\frac{d^2E}{dR_K dF_i} \\ \frac{d\alpha_{ij}}{dR_K} &= -\frac{d^3E}{dR_K dF_i dF_j} \end{aligned} \tag{2.5}$$

Here mixed second and third order derivative of energy with respect to homogeneous electric field and geometry are obtained by numerical differentiation of analytically calculated dipole moment and polarizability with respect to the co-ordinates.

In particular, we perform for each atom and each co-ordinate x, y and z two different displacements by the small distance (x = 0.001 a.u.) in the positive and negative direction of current axis. Though because of this semi-numerical approach the number of calculations increases, this scheme gives scope of coarse grain parallelization. Further, use of molecular symmetry brings down the number of calculations to a manageable one. Numerical differentiation demands a high precision in convergence to obtain accurate intensity. We put 10^{-10} a.u. cut off on energy to minimize numerical error.

The SCF, MP2 and non-variational CCSD (SRCCSD) calculations are done using Gaussian09 [43]. FCI values are obtained using GAMESS [44].

2.3 Results and discussion

In this chapter we present IR and Q branch Raman spectroscopic properties for hydrogen fluoride, boron hydride, carbon monoxide, formaldehyde and carbon monohydride cation as test molecules using ECC functional. IR and Raman intensities are derivatives of the dipole moment and polarizability with respect to the nuclear co-ordinates and are obtained using semi-numerical approach. Dipole moment and polarizabilities are calculated analytically using static approximation without freezing any core orbitals. The double linking of the ECC functional ensures that the properties obtained are always size extensive at each truncation. We have used singles and doubles approximation and a quadratic truncation of the left exponential in our study. For all the molecules we have studied the effect of triples through inclusion of partial triples, as explained before. Hydrogen fluoride has been studied extensively in ten different basis sets starting from a DZ basis to the aug-cc-pVQZ basis. We benchmark IR and Raman intensities along with the vibrational frequency and depolarization ratio for HF molecules in DZ basis [45] with the available full CI (FCI) results. We have used cc-pVTZ basis set [46,47] for all the molecules except hydrogen fluoride and formaldehyde. To have the proper understanding of the basis set effects we have studied HF, BH and CH^+ in aug-cc-pVQZ basis.

We compare our results of IR and Raman properties with analytic CCSD results available for HF molecule [42] in Sadlej basis set [48,49]. In the case of formaldehyde, calculations are performed using Sadlej basis set [48,49]. All studies are done at the experimental geometry, with the exception of hydrogen fluoride in Sadlej basis, where calculations are done at the geometry (r_e = 1.7480 a.u.) are reported [42] for the purpose of comparison. We also report the CCSD (T) basis set limit results for comparison [36] for hydrogen fluoride and carbon monoxide.

2.3.1 Hydrogen fluoride

We have studied the basis set convergence of IR and Raman spectroscopic properties for HF. We have chosen DZ basis set and then gradually added Pople's polarization functions [50] up to 2p + 1d for the hydrogen and 2d + 1f for the fluorine atom to reach the expansion limit. A similar exercise was done with the triple zeta basis set to study the effect of valence orbitals along with the polarization. Results are presented in Table 2.1. It can be seen that, the vibrational frequency is reduced by 62 cm^{-1} with the addition of polarization function. Further with the addition of p and d functions of more diffuse character, frequency is reduced by 91 cm^{-1}. In this basis i.e. DZ + 2p we get vibrational frequency of 4137 cm^{-1} which is very close the experimental value of 4138.32 cm^{-1}. Further addition of polarized function overestimates the frequency. IR intensity as well as depolarization ratio increases from DZ to DZ + p basis, but the trend is just the opposite for Raman intensity. The IR intensity in DZ basis is 33 (km-mol^{-1}) and increases to 108 (km -mol^{-1}), with further addition of p and d functions it keeps on decreasing. Except for the IR frequency we do not have experimental results available for any other property for comparison. To study the effect of valence basis set, we carried out a similar study for the triple zeta (TZ) basis set. IR frequency reduces by 72 cm^{-1}, as we go from DZ to TZ basis. This change is comparable to the addition of a polarization function. With the addition of successive polarization functions, IR frequency approaches the experimental value. The effect of addition of polarization function in TZ basis is less compared to the DZ basis. It can be seen that as we go from DZ to TZ basis IR intensity is enhanced by 98 (km- mol^{-1}). However, with the addition of successive polarization functions, it approaches the value of 108 (km- mol^{-1}), which is slightly higher than the DZ + 3P basis. Raman intensity is not affected much with the valence basis set. Thus, from the basis set convergence study it can be seen that for the accurate description of IR frequency we need a proper combination of valence as well as polarization functions.

Table 2.1 HF Properties basis set convergence study (r_e=1.7328 a.u.)

Property	**ω (cm^{-1})**	**I^{IR} (km-mol^{-1})**	**I^{Raman} (Å^4/ AMU)**	**ϱ**
DZ	4291	33	44	0.41
DZ+P(H-1p/F-1d)[a]	4228	108	37	0.37
DZ+2P (H-2p/F-2d)[b]	4137	103	35	0.27
DZ+3P(H-2p,1d/F-2d,1f)[c]	4148	100	33	0.24
TZ	4219	131	41	0.38
TZ+P(H1p/F1d)[a]	4162	104	34	0.35
TZ+2p(H-2p/F-2d)[b]	4144	108	32	0.30
TZ+3p(H-2p,1d/F-2d,1f)[c]	4132	108	31	0.27
Expt c	4138.32	-	-	-

a H α_p=1.0; Fα_d=1.75.; b H α_p=0.1875; Fα_d=0.8.; c α_d=1.0; Fα_f=1.65; d: see ref [51]

We benchmark our results with the FCI only in DZ basis set. Table 2.2 reports spectroscopic properties in DZ basis. We can see that our IR frequency value 4291 cm^{-1} is just 4 cm^{-1} higher com-pared to a FCI value of 4287 cm^{-1}. Similarly, IR and Raman intensities are in good agreement with the FCI value. The depolarization ratio in ECCSD is 0.41 whereas FCI value is 0.39 which is also in good agreement. Thus, it can be seen that our results are in good agreement with the FCI values.

Table 2.2 Properties of HF in DZ basis (r_e=1.7328 a.u.)

Property	ECCSD	FCI
E (a.u.)	-100.1583	-100.3474
μ (D)	2.285	2.282
α_{zz} (a.u.)	4.22	4.14
α_{xx}(a.u.)	0.80	0.80
ω (cm^{-1})	4291	4287
I^{IR} (km- mol^{-1})	33	34
I^{Raman} (Å^4/ AMU)	43	44
ϱ	0.41	0.39

Table 2.3 reports Raman spectroscopic properties of hydrogen fluoride molecule in Sadlej basis set. We compare our results with the available SRCCSD results. Here geometry is taken from Ref. [42] which is slightly different from the experimental geometry. Comparing our results in DZ and Sadlej basis set, we observe that with improvement in the basis, frequency goes towards the experimental limit. SRCCSD and ECCSD vibrational frequencies are 4113 cm^{-1} and 4117 cm^{-1}, compared to the experimental frequency [51] value of 4138.32 cm^{-1}. The Raman intensity is not affected by the basis set. However, depolarization ratio, which is the ratio of the peak intensity of the parallel and perpendicular component of Raman scattered light, is affected by the basis set. In DZ basis depolarization ratio is 0.41 whereas, in Sadlej basis it is 0.13. From Table 2.3, it can be seen that IR frequency, Raman intensity and the depolarization ratio are in good agreement with each other in ECCSD and SRCCSD approach. It should be mentioned here that ours is semi-numerical approach whereas, results obtained using SRCCSD in Ref. [42] are fully analytic. Thus, it can be seen that for small diatomic molecules semi-numerical approach gives good agreement with the full analytic approach.

Table 2.3 HF properties in Sadlej basis (r_e=1.7485 a.u.)

Property	**ECCSD**	**SRCCSD**[a]	**Experiment**[b]
ω (cm^{-1})	4117	4113	4138.32
I^{Raman} (Å^4/ AMU)	44.09	43.67	-
ϱ	0.13	0.12	-

[a] *see Ref. [42];* [b] *see Ref [51]*

Table 2.4 reports spectroscopic properties of hydrogen fluoride molecule in aug-cc-pVQZ basis set. We compare our IR frequencies with the experimental as well as available basis set limit value for CCSD (T) in parenthesis. It can be seen from the Table 2.4 that our results for dipole moment [52], polarizability [53], IR frequency and intensity are in good agreement with the CCSD values. Vibrational frequency using CCSD is 4157 cm^{-1}, ECCSD gives 4153 cm^{-1} which is just 4 cm^{-1} lower. With the inclusion of partial triples we get 4147 cm^{-1} which is in good agreement with the basis set limit value of 4146.6 cm^{-1} for CCSD (T) method. Though, our vibrational frequency value is 9 cm^{-1} higher compared to experimental value of 4138.32 cm^{-1}, it is more appropriate to compare it with the basis set limit value. Similarly, IR intensity value using ECCSD is 114 (km -mol^{-1}) and using SRCCSD it is 112 (km- mol^{-1}). Inclusion of partial triples reduces IR intensity to 105 (km- mol^{-1}). However, for Raman intensity and depolarization ratio we do not have any experimental or theoretical results available for comparison. So we have compared our calculated value of geometrical derivative of isotropic polarizability with the numbers reported by Pecul and Rizzo [40] and corresponding experimental value [54]. It can be seen that our value of 2.9 a.u. is in good agreement with that of Pecul and Rizzo (3.0 a.u). But both values deviate a little from the experimental value of 3.6 a.u. Here it should be kept in mind that both the values are calculated within in the double harmonic approximations and anharmonic corrections are probably necessary for getting the experimental accuracy.

Table 2.4 HF aug-cc-pVQZ Results (r_e=1.7328 a.u.)

Property	SCF	MP2	SRCCSD	ECCSD	ECCSD(T)	Expt.
E (a.u.)	-100.0685	-100.3697	-100.3691	-100.4093	-100.4094	-
μ (D)	1.922	1.805	1.814	1.818	1.798	1.826[a]
α_{zz} (a.u.)	5.74	6.34	6.20	6.13	6.26	6.40[b]
α_{xx}(a.u.)	4.42	5.17	4.96	4.98	5.07	5.08[b]
ω (cm^{-1})	4162	4163	4157	4153	4147(4146.6)[c]	4138.32[d]
I^{IR} (km- mol^{-1})	168	113	112	114	105	-
I^{Raman}(Å^4/ AMU)	34	39	-	31	32	-
$\left(\frac{d\alpha}{dr}\right)_{R_0}$ a.u.	-	-	-	2.8	2.9(3.0[e])	3.6[f]
ϱ	0.26	0.20	-	0.61	0.43	-

[a] See Ref. [52]; [b] See Ref. [53]; [c] Complete basis set limit value for CCSD(T). See Ref. [36]; [d] See Ref. [51].; [e] Value calculated by Pecul et. al. at the CC3(frozen core)/aug-ccpVTZ level. See Ref. [41].; [f] See Ref. [54]

2.3.2 Boron hydride

Boron hydride is studied for IR and Raman properties in cc-pVTZ and aug-cc-pVQZ basis. Tables 2.5 and 2.6 report all the property values in cc-pVTZ and aug-cc-pVQZ basis respectively. We also report all the properties using SCF and MP2 along with ECCSD method. For BH molecule, only experimental results available are for IR frequency. Hence, we have used Gaussian 09 software to benchmark our ECCSD results with CCSD calculations. We can see that the energy, dipole moment [55], parallel and perpendicular component of the polarizability are in good agreement with the CCSD results. With the inclusion of electron correlation IRfrequency is reduced from SCF to MP2 to CCSD. In both the basis sets we have studied the effect of partial triples for IR as well as Raman properties. It can be seen that the effect of partial triples on IR intensities as well frequencies is very little in both the basis sets. However, the effect of basis set is quite large. For frequencies it is 12 cm^{-1} and for the case of intensity it is 18 (km -mol^{-1}). The vibrational frequency in cc-pVTZ basis set in ECCSD is 2346 cm^{-1}, where as in aug-cc-pVQZ basis we get 2358 cm^{-1}. Thus, with the basis set improvement we approach the experimental value 2366 cm^{-1}. In aug-cc-pVQZ basis ECCSD (2358 cm^{-1}) and SRCCSD (2359 cm^{-1}) IR frequencies agree well with each other. Though, we are still away from the experimental [51] (2366 cm^{-1}) value by 8 cm^{-1}. This may be due to harmonic approximation. With the inclusion of triples frequencies are reduced and correction is away from the experimental value. Raman intensities are not affected by the basis set. In cc-pVTZ the value of Raman intensity is (226 Å^4/AMU) where as in aug-cc-pVQZ basis it is (223 Å^4/AMU), with the inclusion of triples it is increased to 241 Å^4/AMU. Depolarization ratio is reduced to 0.53 in QZ basis from 0.69 in TZ basis. Triples have marginal effect on the depolarization ratio giving the value of 0.54 in QZ basis and 0.60 in TZ basis. Thus, except for Raman intensity triples has marginal effect on the rest of the properties in aug-cc-pVQZ basis.

Table 2.5 BH cc-pVTZ Results (r_e=2.3289 a.u.)

Property	**SCF**	**MP2**	**SRCCSD**	**ECCSD**	**ECCSD(T)**	**Exp.**
E (a.u.)	-25.1299	-25.2034	-25.2285	-25.2390	-25.2391	-
μ (D)	1.725	1.571	1.368	1.392	1.365	1.2708[a]
α_{zz} (a.u.)	21.09	21.23	21.50	22.10	22.03	-
α_{xx}(a.u.)	19.97	19.37	18.10	18.81	18.05	-
ω (cm^{-1})	2420	2397	2373	2346	2343	2366[b]
I^{IR}(km- mol-1)	406	385	378	375	370	-
I^{Raman}($Å^4$/AMU)	238	229	-	226	234	-
ϱ	0.76	0.75	-	0.69	0.60	-

[a]*See Ref. [55];* [b]*See Ref. [51]*

Table 2.6 BH aug-cc-pVQZ Results (r_e=2.3289 a.u.)

Property	**SCF**	**MP2**	**SRCCSD**	**ECCSD**	**ECCSD(T)**	**Exp.**
E (a.u.)	-25.1313	-25.2097	-25.2331	-25.2674	-25.2675	-
μ (D)	1.740	1.614	1.411	1.368	1.345	1.270[a]
α_{zz} (a.u.)	22.89	22.94	23.02	22.98	23.08	-
α_{xx}(a.u.)	22.54	22.42	20.80	20.85	20.87	-
ω (cm^{-1})	2411	2388	2359	2358	2354	2366[b]
I^{IR}(km-mol^{-1})	422	402	409	393	390	-
I^{Raman}(Å^4/AMU)	243	240	-	223	241	-
ϱ	0.74	0.73	-	0.53	0.54	-

[a] *See Ref. [55].*; [b] *See Ref. [51].*

2.3.3 Carbon mono-hydridecation

Carbon mono-hydride cation is studied for spectroscopic properties using cc-pVTZ and aug-cc-pVQZ basis set. Tables 2.7 and 2.8 reports SCF, MP2 along with CC results in cc-pVTZ and aug-cc-pVQZ basis set respectively. Since, there are no experimental or theoretical results available for comparison , we have compared our IR frequencies, intensities along with energy, dipole moment and polarizability with the SRCCSD results. It is seen that with the inclusion of correlation, IR intensity and frequency are reduced. ECCSD and SRCCSD agree well with each other for dipole moment, polarizability and IR properties. We also report all the property values with the partial inclusion of triples in both the basis sets. It can be seen that the effect of triples on IR frequency is less in cc-pVTZ basis, whereas in aug-cc-pVQZ basis IR frequency is changed by 16 cm^{-1}. IR intensities are unaffected by the inclusion of triples in both the basis sets. As we go from TZ to QZ basis the frequency changes by 42 cm^{-1} in CCSD approximation and 32 cm^{-1} with triples correction, which is a large change. Raman intensity is margin-ally affected by the inclusion of triples in both the basis sets. However, as we go from cc-pVTZ basis (58 (km-mol^{-1})) to aug-cc-pVQZ basis (44 (km-mol^{-1})) in CCSD approximation Raman intensity value is increased by 8 (km-mol^{-1}). The depolarization is increased from 0.40 to 0.65 as we go from TZ to QZ basis set. Inclusion of triples reduces it to 0.41 in aug-cc-pVQZ basis.

Table 2.7 CH+ cc-pVTZ Results (r_e=2.137 a.u.)

Property	**SCF**	**MP2**	**SRCCSD**	**ECCSD**	**ECCSD(T)**
E (a.u.)	-37.9074	-37.9921	-38.0214	-38.0337	-38.0338
μ (D)	1.576	1.598	1.235	1.696	1.675
α_{zz} (a.u.)	8.05	8.21	8.17	8.43	8.44
α_{xx}(a.u.)	7.25	7.04	6.86	6.71	6.73
ω (cm^{-1})	2921	2890	2862	2814	2808
I^{IR}(km-mol^{-1})	7	3.2	1.6	1.7	1.8
I^{Raman}($Å^4$/AMU)	61	62	-	58	59
ϱ	0.52	0.51	-	0.40	0.34

Table 2.8 CH+ aug-cc-pVQZ Results (r_e=2.137 a.u.)

Property	**SCF**	**MP2**	**SRCCSD**	**ECCSD**	**ECCSD(T)**
E (a.u.)	-37.9094	-38.0005	-38.0279	-38.0635	-38.0683
μ (D)	1.5637	1.475	1.332	1.702	1.168
α_{zz} (a.u.)	8.00	8.15	8.35	8.35	8.36
α_{xx}(a.u.)	7.63	7.44	7.01	7.13	7.15
ω (cm^{-1})	2909	2879	2850	2856	2840
I^{IR}(km-mol^{-1})	7	4	2	2	2
I^{Raman}(Å^4/AMU)	61	62	-	66	61
ϱ	0.46	0.46	-	0.65	0.41

2.3.4. Carbon monoxide

We report the IR and Raman intensity along with IR frequency and depolarization ratio for carbon monoxide. We have used cc-pVTZ and aug-cc-pVTZ basis set [56] for our study. We compare our results with the experimental values for the frequency [57] and IR intensity [58]. We also report the basis set limit value for the IR frequency within CCSD (T) approximation. Table 2.9 reports different properties of CO using ECCSD as well as ECCSD (T) method. The IR frequency value in cc-pVTZ basis using ECCSD method is 2224 cm^{-1}. With the inclusion of partial triples it is reduced to 2208 cm^{-1}. Thus, inclusion of partial triples reduces frequency by 16 cm^{-1}. However, compared to the experimental value of 2170 cm^{-1}, it is still overestimated by 38 cm^{-1}. With the augmentation of the basis, IR frequency is reduced at the ECCSD as well as ECCSD (T) level by 8 cm^{-1}. Compared to the basis set limit values within CCSD (T) approximation 2176.9 cm^{-1} our ECCSD (T) value is 23 cm^{-1} higher. Using aug-cc-pVQZ basis we may be able to reach the basis set limit value. The IR intensity at the ECCSD level in cc-pVTZ basis is 74 (km- mol^{-1}) and with the inclusion of triples it is reduced to 58 (km-mol^{-1}). In aug-cc-pVTZ basis intensity is 77 (km -mol^{-1}) using ECCSD (T) method it is reduced to 64 (km- mol^{-1}). It can be seen that effect of augmentation is negligible compared to effect of inclusion of partial triples for IR intensity. In both basis sets, addition of partial triples brings the value within experimental range. The percentage error in the IR frequency compared to the experimental values is less than 2 percent which is within experimental error bar. To get the experimental accuracy of the frequency, we need to include anharmonic corrections along with triples inclusion. We also report Raman intensities and depolarization ratio in cc-pVTZ basis at CCSD as well as CCSD(T) level. However, there are no theoretical or experimental results available for comparison. But our calculated value of geometrical derivative of isotropic polarizability is in good agreement with the experimental value [59].

Table 2.9 IR and Raman properties of CO (r_e=2.131a.u.)

Basis	Property	ECCSD	ECCSD(T)	Expt.
cc-pVTZ	ω (cm^{-1})	2224	2208	2170[a]
-	I^{IR}(km-mol^{-1})	74	58	51-64[b]
-	I^{Raman}($Å^4$/AMU)	18	10	-
-	$\left(\frac{d\alpha}{dr}\right)_{R_0}$ a.u.	4.54	3.99	5.34
-	ϱ	0.22	0.30	-
aug-cc-pVTZ	ω (cm^{-1})	2215	2200(2176.9[c])	2170
-	I^{IR}(km-mol^{-1})	77	64	51-64
-	I^{Raman}($Å^4$/AMU)	21	17	-
-	$\left(\frac{d\alpha}{dr}\right)_{R_0}$ a.u.	5.84	5.16(6.02[d])	5.34[e]
-	ϱ	0.24	0.34	-

[a] See Ref. [57].[b] See Ref. [58].[c] Complete basis set limit value for CCSD(T). See Ref. [36].[d] Values calculated by Pecul et. al. at the CC3(frozen core)/aug-cc-pVTZ level. See Ref. [41].[e] See Ref. [59].

2.3.5. Formaldehyde

IR intensities and frequencies of formaldehyde are studied using Sadlej basis set. Z axis is molecular axis with both the hydrogens being placed symmetrically on the XZ plane. For formaldehyde we have also studied effect of triples on IR frequency and intensities. We compare our results with the SRCCSD as well as experimental values. Table 2.10 reports energy, dipole moment [60], parallel and perpendicular components of polarizabilities along with IR frequencies [61], intensities for all the six normal modes. In parenthesis are the values with inclusion of partial triples. Experimentally [62] the most intense mode for formaldehyde molecule in the gas phase is the CH_2 asymmetric stretching mode which appears at 3033 cm^{-1}. The C=O stretching mode is the second most intense mode appearing at 1761 cm^{-1}. The CH_2 symmetric stretching mode is also of significant intensity. As compared to these three modes, the remaining three modes are of negligible intensity. To study the effect of correlation, we report SCF, MP2 results along with the coupled cluster. For all the six modes of vibration, correlation decreases IR frequencies and most of the intensities, except for the CH_2 stretching modes. For the CH_2 out of plane bending mode (x_1), coupled cluster method underestimates the frequency by 11 cm^{-1} however, IR intensity is in good agreement with the experimental values. For the CO stretching mode, IR frequency as well as intensity decreases with the electron correlation. However, intensity as well as frequency are overestimated compared to experimental values. We observe that the CO symmetric stretching intensity improves with the inclusion of triples. By using ECCSD IR intensity for this mode is 93 (km -mol^{-1}). With the inclusion of triples, it is reduced to 70 (km-mol^{-1}), which is closer to the experimental value of 74.0 ± 5.3 (km- mol^{-1}). All the intensities are decreased with the inclusion of triples, except for CH_2 symmetric and asymmetric stretch. After inclusion of triples we get IR intensities closer to the experimental values. In general, it is seen that effect of triples is more prominent on IR intensities compared to the frequencies. All the vibrational frequencies are reduced with the inclusion of triples. However, to achieve experimental accuracy use of proper basis set and anharmonic corrections along with the triples might be crucial.

Table 2.11 reports Raman intensities for all six modes of vibrations. Out of six modes of vibrations, CH_2 symmetric and asymmetric stretching modes are Raman active. With the inclusion of correlation, CH_2 symmetric stretching mode intensity increases, whereas asymmetric stretching mode intensity decreases. We do not have any theoretical or experimental values to compare our results. Table 2.9 reports relative Raman intensities of formaldehyde using MP2, ECCSD and experimental values. To The best of our knowledge only experimental data available, comes from the chapter by Wiegeler and Bleckmann [63]. Unfortunately, no details about experimental accuracy are given in Ref. [63]. Hence, in Table 2.12 we compare the experimental values of relative Raman intensities with those obtained at ECCSD method. Our results are in good agreement with the experimental relative Raman intensities except for the CH_2 asymmetric stretching. In case of CH_2 asymmetric stretching also, results are better than the MP2 values calculated in same basis set.

Table 2.10 H_2CO Results (r_{co}=2.274 a.u., r_{ch}=2.079 a.u.,∠ HCO=121.62)

Property	**SCF**	**MP2**	**ECCSD**	**SRCCSD**	**Expt**
E (a.u.)	-113.9010	-114.2270	-114.2755	-114.2419	-
μ (D)	2.832	2.332	2.382	2.378	2.331[a]
α_{zz} (a.u.)	21.186	22.149	18.308	17.497	-
α_{xx} (a.u)	12.234	12.741	13.394	12.547	-
Harmonic	Vibrational	Frequencies	(cm^{-1})		
ω_1 (CH_2 oop bending)	1334	1178	1176(1150)	1172	1187[b]
ω_2 (CH_2 rock)	1340	1237	1238(1224)	1235	1282[b]
ω_3 (CH_2 symm bending)	1608	1517	1512(1499)	1510	1517[b]
ω_4 (C=O symm stretch)	1884	1847	1863(1851)	1864	1761[b]
ω_5 (CH_2 symm stretch)	3096	3061	3057(3048)	3060	2944[b]
ω_6 (CH_2 asymm stretch)	3190	3153	3146(3135)	3148	3033[b]
Infrared	Intensities	(km-mol^{-1})			
I_1^{IR}	4	5	5(6)	5	6.5±0.6[c]
I_2^{IR}	20	11	14(10)	13	9.9±0.6[c]
I_3^{IR}	30	4	6(6)	5	11.2±1.0[c]
I_4^{IR}	141	81	93(70)	92	74.0±5.3[c]
I_5^{IR}	51	74	60(66)	62	75.5±7.1[c]
I_6^{IR}	71	98	90(101)	92	87.6±8.0[c]

[a].SeeRef.[60];[b]See.Ref.[61];[c]SeeRef.[62]

Figure 2.1 Vibrational modes of formaldehyde (H_2CO)

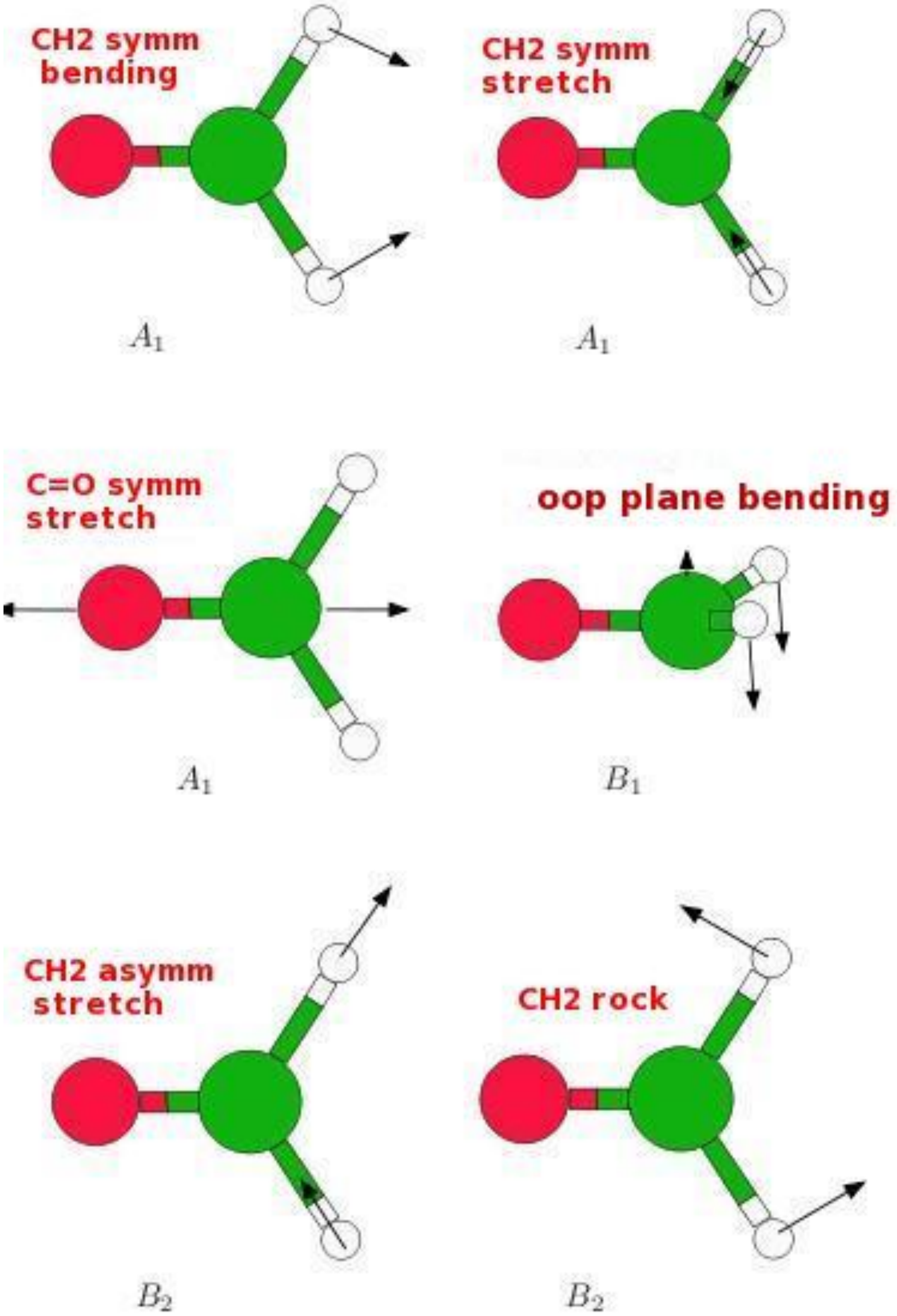

Table 2.11 H_2CO Raman Intensities in Sadlej Basis ($Å^4$/AMU)

Property	SCF	MP2	ECCSD
I_1^{Raman}	0.05	0.30	0.06
I_2^{Raman}	0.88	0.94	1.52
I_3^{Raman}	9.56	8.96	8.66
I_4^{Raman}	15.01	8.48	10.98
I_5^{Raman}	148.01	184.95	178.51
I_6^{Raman}	65.45	97.81	61.52

Table 2.12 H_2CO comparison of experimental and theoretical relative Raman intensities

(Expressed as percentage)

Method	$\boldsymbol{\omega_1}$	$\boldsymbol{\omega_2}$	$\boldsymbol{\omega_3}$	$\boldsymbol{\omega_4}$	$\boldsymbol{\omega_5}$	$\boldsymbol{\omega_6}$
MP2(Sadlej)	<1	<1	5	5	100	53
ECCSD (Sadlej)	<1	<1	5	6	100	34
Experimental[a]	1	3	10	8	100	2

a See Ref. [63].

2.4. Conclusion

In this chapter we focus on the calculation of IR and Q branch of Raman intensity as well as depolarization ratios of small molecules using ECC method. We have used ECCSD approximation in which left exponential is truncated up to quadratic terms. We have implemented partial triples in non -iterative manner. The double linked nature of the functional ensures that the properties are always size extensive up to all the orders. Determination of IR and Raman intensities by ab initio methods requires the calculation of the di-pole moment and polarizability derivative with respect to the geometry. We have implemented semi-numerical approach for obtaining IR and Raman intensities. Reliable calculations of the geometric derivatives of the molecular polarizability require a good description of electron correlation. These derivatives are useful for the calculation of Raman scattering cross section. The depolarization ratio provides information about the symmetry of the vibrations. We have also studied the effect of partial triples on IR properties of all the molecules. Raman intensities and depolarization ratios are studied with the inclusion of partial triples for all molecules except formaldehyde. In particular HF, BH and CH^+ are studied in aug-cc-pVQZ basis to know how the inclusion of partial triples affects IR and Raman properties. We observe that vibrational frequencies are marginally changed by the inclusion of partial triples for HF and BH. However, for CH^+ inclusion of partial triples reduces IR frequencies by 16 cm^{-1}. For hydrogen fluoride we obtained the IR frequency value 4147 cm^{-1} in aug-cc-pVQZ ba-sis which is close the basis set limit value 4146.6 cm^{-1} for CCSD (T). IR intensities are unaffected for BH and CH^+, whereas for HF molecules the change is about 9 (km-mol^{-1}) after the inclusion of triples. Raman intensity for BH is increased by 18 (Å^4/AMU), whereas HF and CH^+ are Raman intensities are unaffected. Depolarization ratio is very sensitive to the inclusion of triples for HF and CH^+, however, for BH there is no change. For CO and H_2CO effect of partial triples is more prominent. In case of CO, we have also studied the effect of augmentation of basis set by using cc-pVTZ and aug-cc-pVTZ basis. We observe that augmentation has little effect on intensity. However, frequencies are changed by about 8 cm^{-1}. Inclusion of partial triples changes the frequency by about 15 $cm^{–1}$. Thus, effect of partial triples is more than the augmentation of basis set for CO. In case of IR intensity, triples reduce CCSD intensities by almost 17 percent, making it closer to the experimental value. Similarly, for formaldehyde, we observe that for the CO symmetric stretch mode, IR intensity is reduced by 23 percentage, with the inclusion of partial triples. The other two stretching modes of CH_2 are marginally affected by the inclusion of partial tri-ples. Within harmonic approximation, our results are quite accurate for the IR frequencies. From our results, it can be seen that inclusion of partial triples along with aug-cc-pVQZ basis gives accurate spectroscopic properties. It is difficult to discuss the quality of calculated Raman activities due to lack of experimental data, but our results are consistent with available theoretical values.

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Chapter 3

Multipole moments using extended coupled cluster method

Using analytic extended coupled cluster (ECC) response approach quadrupole moments, dipole–quadrupole polarizabilities and dipole polarizabilities are studied. In the current implementation of the functional we have included all the double linked terms within (CCSD) approximation. These terms will be important for the accurate description of properties at the stretched geometries. We report the properties for carbon monoxide and hydrogen fluoride molecules, as a function of bond distance and compare our results for carbon monoxide with the full CI results. We have also reported the properties of methane, tetrafluoromethane, acetylene, difluoroacetylene, water and ammonia.

3.1 Introduction

Among various *ab initio* methods single reference coupled cluster method (SRCC) [1] is best suited for the accurate calculation of energy [2] and energy derivatives [3–5] of the molecules in their ground state. The success of the theory lies in its ability to introduce electron correlation accurately even in its approximate form. Various forms of the SRCC method have enabled the accurate calculation of molecular properties, gradients, geometry optimization and potential energy surfaces at equilibrium or near equilibrium geometry.

First order properties, i.e. dipole moment, quadrupole moment can be obtained using expectation value method. A more general approach is the response approach [3] which is used for the calculation of higher order properties. With the help of Z vector technique [6,7], SRCC method can be used for the calculation of properties. However, this approach is difficult to extend for higher order properties. Constrained variation approach of Jørgensen and co-workers [8] is based on Lagrange multipliers and can be easily extended for higher order properties. The resulting equations using constrained variational approach are same as the one obtained by non-variational Z-vector technique for the first order properties.

Pal et al. [9] developed a stationary response approach. In a variational/stationary approach a suitable energy functional is chosen, which is made stationary with respect to the cluster amplitudes. This method is most suitable for the calculation of energy derivatives, in particular higher order derivatives because of the inbuilt ($2n + 1$) rule. In this approach, the choice of the energy functional is very crucial. Pal and co-workers [10, 11] used different energy functionals namely, expectation value coupled cluster (XCC), unitary coupled cluster (UCC) and extended coupled cluster (ECC) for the calculation of properties. Among the various functionals, ECC [12, 13] was found to be most suitable for the calculation of molecular properties due to its double linked nature resulting in a naturally terminating series. This functional was used for the calculation of electric [11, 14] as well as magnetic properties [15, 16] of small molecules. The initial implementation was based on the cubic truncation scheme. In the current implementation we have used the right as well as left vector all the terms within singles and doubles approximation which are double linked. We denote them as cubic-ECCSD and ECCSD throughout the chapter. The terms included are expected to be important for the property calculations at the stretched geometry.

Electric properties in particular have been studied very extensively due to their role in the design of non-linear optical materials [17–21]. On the other hand dipole–quadrupole polarizabilities [22] and dipole–octupole polarizabilities [23, 24] have recently received attention. They are important for the Raman scattering studies as well as interaction induced light scattering spectra. The gradient of the dipole–quadrupole polarizability are important for the determination of vibrational Raman optical activity (VROA) intensities.

Study of multipole moments [23, 24] is important due to their applicability in predicting long range interactions [25] in atoms and molecules. Unlike the dipole moments which can be experimentally measured, experimental measurement of quadrupole moments depends on various parameters. High quality *ab initio* calculations, is the best way to obtain accurate values of quadrupole moments. In this chapter we report the study of basis set and electron correlation on quadrupole moment, dipole–quadrupole polarizability and dipole polarizability, of small molecules. We report the properties of carbon monoxide and hydrogen fluoride as a function of bond length to emphasize the importance of the terms newly added in the functional. We have also studied methane, tetrafluoromethane, acetylene, difluoroacetylene, water, and ammonia as a case study. The chapter is organized as follows. Section 3.2 gives brief theory of the ECC response properties. Results and discussion on them will be presented in Section 3.3. Section 3.4 contains conclusions.

3.2 Theory

To obtain the properties of our interest, we have used the ECC functional. The ECC functional uses different ket and conjugate vectors.

$$\langle H \rangle = \langle \Psi' | H | \Psi \rangle \tag{3.1}$$

where $|\Psi\rangle$ and $\langle\Psi'|$ are parameterized differently and are bi-orthogonal to each other. This functional also known as the ECC functional, was first proposed by Arponen and Bishop [12, 13]. After double similarity transformation the form of the functional is given as follows

$$\langle H \rangle = \langle \Phi_0 | e^{\Sigma} (He^{T})_L | \Phi_0 \rangle_{DL} \tag{3.2}$$

Here subscript L denotes the T operator to the right of Hamiltonian, which is linked /connected to H, subscript DL (double linked) means the left operator Σ is either connected to the Hamiltonian H or to two different T operators. Double linking ensures that the series is naturally terminating and hence gives size-extensive properties [11]. ECC method differs from the standard SRCC due to presence of left exponential, which includes several higher order terms. In this chapter, the contribution of right vector is taken full within CCSD approximation i.e. (He^T) and all the higher order terms within CCSD approximation are included in the left vector. The extra terms that are included in the energy functional are $\Sigma_2 V T_2 T_1^2, \Sigma_2 V T_1^3, \Sigma_2 V T_1^4, \Sigma_1^3 V T_2$.

The cluster amplitudes are obtained using following equations

$$\frac{\delta E}{\delta t^{(0)}} = 0; \frac{\delta E}{\delta \sigma^{(0)}} = 0 \tag{3.3}$$

Similarly, the derivative energy functional $E^{(1)}$ is obtained by replacing either the Hamiltonian by derivative Hamiltonian, i.e. dipole operator/ quadrupole operator or one of the cluster operator by its derivative

$$E^{(1)} = \langle \Phi_0 | e^{\Sigma} (He^{T})_L | \Phi_0 \rangle_{DL} + \langle \Phi_0 | e^{\Sigma} [\Sigma^{(1)} (He^{T})_L + (He^{T} T^{(1)})_L | \Phi_0 \rangle_{DL} \tag{3.4}$$

where, the T and its derivative $T^{(1),}$ are explicitly connected to the Hamiltonian derivative or to the Hamiltonian. Similarly, the Σ or its derivative $\Sigma^{(1)}$, will either be connected to the Hamiltonian derivative or to the Hamiltonian or to two different T operators. To obtain the derivative amplitudes, the derivative functional is made stationary with respect to the amplitudes of Σ and T operators. For example, the first derivative amplitudes of Σ and T operators are obtained by the solution of the following set of equations.

$$\frac{\delta E^{(1)}}{\delta t^{(0)}} = 0; \frac{\delta E^{(1)}}{\delta \sigma^{(0)}} = 0 \tag{3.5}$$

Equations (3.3) and (3.5) define the amplitude and derivative amplitude equations. With the help of them we can obtain the properties up to third order using Hellmann–Feynman theorem. The dipole and quadrupole moments are obtained as the expectation values of the dipole and quadrupole moment operator. However, second order properties like the dipole polarizability, dipole–quadrupole polarizability are obtained using analytic response approach.

3.3 Results and discussion

We report the quadrupole moment, dipole–quadrupole polarizability and dipole polarizability using ECCSD method. Dipole–quadrupole polarizability is evaluated for methane, tetrafluoromethane, water, ammonia, carbon monoxide, hydrogen fluoride while quadrupole moments of acetylene, difluoroacetylene, water, ammonia and carbon monoxide are calculated. Dipole polarizability is calculated and reported for all the molecules. We have used cc-pVDZ and aug-cc-pVDZ basis [26] for all the molecules except for carbon monoxide we have used DZ (dunning) basis set. Water molecule has also been studied using Sadlej basis set [27] to compare our analytical values with the other correlated methods. All the calculations are done at the equilibrium geometry except for carbon monoxide and hydrogen fluoride molecule. We compare our results with the available experimental values and/ or with time dependent Hartree–Fock (TDHF) results wherever available. We also report analytic CCSD values for dipole polarizability obtained using DALTON software [28] and quadrupole moment using

GAMESS [29]. For dipole–quadrupole polarizability we compare our results with finite field CCSD values obtained using GAMESS [29].

3.3.1 Comparison between cubic-ECCSD and ECCSD

As mentioned in the previous section, the initial implementation of the functional was based on the cubic approximation, i.e. total of three cluster amplitudes in the functional. In the current chapter we have considered all the terms that appear within CCSD approximation. At the equilibrium geometry, these terms are not expected to contribute much in the property calculations. However, at the stretched geometry we expect them to improve the results. In particular, higher order properties should show improvement. To confirm our point we have calculated the properties for carbon monoxide and hydrogen fluoride at different geometries. Carbon monoxide molecule was studied using double zeta basis at R_e, 1.25R_e and 1.4R_e. We compare our results with finite field FCI and CCSD values using GAMESS. We also compare quadrupole value for carbon monoxide with the experimental value [30]. For hydrogen fluoride molecule we have used cc-pVDZ basis set. We report the values for R_e, 1.25 R_e, 1.5 R_e, 1.75R_e and 2.00 R_e. For hydrogen fluoride molecule, we compare our results with the finite field CCSD values obtained using GAMESS [29]. In Table 3.1 we report the properties of carbon monoxide at different geometries using cubic truncation and CCSD approximation. We have frozen two core orbitals in our calculations. At the equilibrium as well as at 1.25 R_e , the difference between cubic-ECCSD and ECCSD is marginal. However, effect can be seen that at 1.4Re for dipole polarizability and dipole-quadrupole polarizability. The quadrupole moment has marginal effect of the ECCSD terms. Dipole polarizability values along the molecular axis approaches the CCSD value with ECCSD approximation. Full CI is slightly low compared to ECCSD as well as CCSD value. Dipole–quadrupole polarizability along the molecular axis approaches the Full CI as well as CCSD value with ECCSD values. The effect is prominent for polarizability α_{zz} at 1.4 Re. Similar trend is observed for dipole-quadrupole polarizability of CO along the molecular axis. Carbon monoxide is also studied by Maroulis et. al. [31] and the results obtained for the properties show similar trend using different basis sets.

We have also carried out similar study of comparison between cubic-ECCSD and ECCSD for hydrogen fluoride molecule at R_e, $1.25R_e$, $1.5R_e$, $1.75R_e$ and $2.0R_e$. We compare our results with the finite field CCSD results using GAMESS [29]. We compare our results at the equilibrium geometry with the experimental values [32–34]. In Table 3.2 we report the dipole polarizability and dipole–quadrupole polarizability along the molecular axis. It can be seen that till $1.5R_e$ the difference between the cubic-ECCSD and ECCSD is marginal. At $1.75R_e$ and $2.0R_e$ the dipole polarizability values along the molecular axis differ. Similarly cubic-ECCSD and ECCSD dipole–quadrupole polarizability show a large change and ECCSD approaches FF-CCSD values. The difference between the ECCSD and FF-CCSD is due to relaxation.

Table 3.1 Properties of carbon monoxide in a.u. using DZ (Dunning) basis.

R	Property	SCF	Cubic-ECCSD	ECCSD	SRCCSD	Full CI	Expt.
R_e	α_{zz}	12.88	13.72	13.77	13.91[a]	13.79	-
	A_{zzz}	-9.12	-11.57	-11.57	-11.79[b]	-11.90	-
	Θ_{zz}	-2.283	-2.255	-2.256	-2.256[c]	-2.257	1.44±0.3[d]
1.25 R_e	α_{zz}	18.95	21.08	21.22	21.94[a]	20.51	-
	A_{zzz}	-10.92	-15.29	-15.31	-15.66[b]	-16.02	-
	Θ_{zz}	-1.745	-1.625	-1.625	-1.620[c]	-1.615	-
1.4 R_e	α_{zz}	22.92	28.01	27.53	27.34[a]	25.04	-
	A_{zzz}	-13.561	-18.88	-19.16	-19.18[b]	-19.85	-
	Θ_{zz}	-1.345	-1.091	-1.107	-1.088[c]	-1.147	-

[a] Dalton CCSD results; [b] Finite field results.; [c] See Ref. [29]; [d] See Ref. [30].

Table 3.2 Properties of hydrogen fluoride in a.u. using cc-pVDZ basis.

R	Property	SCF	Cubic-ECCSD	ECCSD	SRCCSD	Expt. Or Correlated
R_e	α_{zz}	4.04	4.171	4.172	4.03[a]	6.428[c] 6.438[e]
	A_{zzz}	4.525	4.758	4.766	4.504[b]	4.508[d]
1.25 R_e	α_{zz}	7.11	7.274	7.267	7.12[a]	-
	A_{zzz}	10.968	11.535	11.515	10.990[b]	-
1.5 R_e	α_{zz}	11.91	12.21	12.13	12.03[a]	-
	A_{zzz}	23.688	25.35	25.00	23.945[b]	-
1.75 R_e	α_{zz}	18.43	19.31	18.79	18.68[a]	-
	A_{zzz}	44.78	50.08	47.28	45.47[b]	-
2.00 R_e	α_{zz}	26.34	27.66	25.74	17.22[a]	-
	A_{zzz}	75.32	86.29	72.91	76.05[b]	-

[a] Dalton CCSD results; [b] Finite field results; [c] CCSD+T(4) see Ref. [32]; [d] MCSCF see Ref. [33]; [e] CCSD(T) see Ref. [34].

3.3.2 Methane and Tetrafluoromethane

Table 3.3 reports the average polarizability and the A_{xyz} component of the dipole–quadrupole polarizability of methane and tetrafluoromethane molecule. The bond length of CH is taken as 1.085 Å [35]. For tetrafluoromethane the bond length is taken as 1.32 Å [36,37]. We compare our results with SRCCSD and TDHF [38] values. Maroulis et al. [39] recommended the best theoretical value for the dipole–quadrupole polarizability for both molecules. Experimental results are available for the A_{xyz} component of tetrafluoromethane. It can be seen that dipole polarizability as well as dipole–quadrupole polarizability values in all the three methods are in good agreement with each other for methane in both the basis sets. With the augmentation of the basis dipole polarizability is enhanced whereas dipole–quadrupole polarizability is reduced for methane. Our results for A_{xyz} in aug-cc-pVDZ basis for methane is in good agreement with the best theoretical results available. Dipole polarizability as well as dipole–quadrupole polarizability values of tetrafluoromethane using ECCSD method are in agreement with SRCCSD. However, TDHF predicts slightly lower values compared to both the CC results. Here too we observe the same trend that with the augmentation of the basis set dipole polarizability is enhanced whereas dipole-quadrupole polarizability is reduced.

Table 3.3 Properties of methane and tetrafluoromethane in a.u.

Molecule	**Basis**	**Property**	**ECCSD**	**SRCCSD**	**TDHF**	**Best (Theory)**	**Expt.**
Methane	cc-pVDZ	$\tilde{\alpha}$	12.73	12.83[a]	13.01[c]	-	-
	aug-cc-pVDZ	$\tilde{\alpha}$	16.14	16.39[a]	16.00[c]	-	-
	cc-pVDZ	Axyz	13.95	14.06[b]	14.40[c]	-	-
	aug-cc-pVDZ	Axyz	9.10	9.14[b]	9.48[c]	9.01[d]	-
Tetrafluoro methane	cc-pVDZ	$\tilde{\alpha}$	12.00	12.39[a]	10.98[c]	-	-
	aug-cc-pVDZ	$\tilde{\alpha}$	18.06	18.85[a]	16.16[c]	-	-
	cc-pVDZ	Axyz	15.08	15.37[b]	12.83[c]	-	-
	aug-cc-pVDZ	Axyz	12.79	13.19[b]	10.94[c]	12.4[d]	12.75[e]

[a] *Dalton CCSD results ;*[b] *Finite field results;* [c] *See Ref. [38];* [d] *See Ref. [39];* [e] See Ref.[36].

3.3.3 Acetylene and difluoroacetylene

The experimental geometry of the acetylene is R_{CC} = 1.0605 Å and R_{CH} = 1.203 Å [40] chosen for the calculations. Geometry of the difluoroacetylene is taken as R_{CC}=1.186 Å and R_{CF} =1.2835 Å [41]. Table 3.4 gives the quadrupole moment and dipole polarizability of both the molecules. It can be seen that the effect of basis set on the quadrupole moment of acetylene is very little. However, electron correlation has relatively larger effect. Our value for quadrupole moment Θ_{zz} in aug-cc-pVDZ basis is in good agreement with the theoretical value [42,43] as well as approaching the experimental value [44]. In case of difluoroacetylene with the augmentation of the basis set Θ_{zz} value becomes almost double using ECCSD as well as SRCCSD. However, SCF value is marginally changed with the basis set. It can also be seen that replacing H by F atom sign of the Θ_{zz} is reversed as well as the value is also reduced. ECCSD values are in good agreement with the SRCCSD values. Dipole polarizability values are enhanced with the augmentation of the basis set. In particular the perpendicular component shows large basis set effect. Effect of electron correlation is relatively more for the component of the polarizability along the molecular axis.

Table 3.4 Properties of acetylene and difluoroacetylene in a.u.

Molecule	Basis	Property	SCF	ECCSD	SRCCSD	Best (Theory)	Expt.
Acetylene	cc-pVDZ	α_{zz}	29.29	27.30	27.81[a]	-	-
		α_{xx}	9.75	9.37	9.50[a]	-	-
		Θ_{zz}	5.20	4.55	4.55[b]	-	-
	aug-cc-pVDZ	α_{zz}	31.35	29.77	30.42[a]	-	-
		α_{xx}	18.55	17.74	17.97[a]	-	-
		Θ_{zz}	5.48	4.81	4.81[b]	4.86[c]	4.55±0.2 (4.57±0.1)[d]
Difluoroacetylene	cc-pVDZ	α_{zz}	28.33	28.95	30.13[a]	-	-
		α_{xx}	10.16	9.88	10.03[a]	-	-
		Θ_{zz}	-0.92	-0.47	-0.50[b]	-0.40[c]	-
	aug-cc-pVDZ	α_{zz}	31.67	32.49	33.83[a]	-	-
		α_{xx}	17.43	17.11	17.52[a]	-	-
		Θ_{zz}	-1.02	-0.96	-0.80[b]	-	-0.78[e]

a Dalton CCSD results.; b See Ref. [39].; c See Ref. [42].; d See Ref. [44].; e See Ref. [35]

3.3.4 Water

We have performed our calculations for water in Sadlej basis set with the geometry of Bishop and Pipin [45]. The two other basis sets considered are cc-pVDZ and aug-cc-pVDZ basis. Table 3.5 reports the property values in Sadlej basis. Here molecule is in XZ plane with Z as a molecular axis. We report the SCF as well as MCSCF values from the Bishop and Pipin's paper [45]. We compare our results with experimental and other theoretical values [46–50]. It can be seen that our results for quadrupole moment, dipole polarizability and dipole–quadrupole polarizability are in good agreement with SRCCSD and other theoretical and experimental values. In Table 3.6 we report the properties using cc-pVDZ and aug-cc-pVDZ basis sets. In cc-pVDZ basis there is not much change in either of the property values as we go from SCF to CC. As we go from cc-pVDZ basis to aug- cc-pVDZ basis dipole polarizability values are enhanced showing the importance of the basis set. Quadrupole moments are enhanced by about 14%. The A_{xxy} component of the dipole–quadrupole polarizability has marginal change, however, A_{yyy} and A_{zyz} components are almost doubled with augmentation of the basis set. For all the values ECCSD is in good agreement with the SRCCSD values.

Table 3.5 Properties of water in a.u. using Sadlej basis.

Property	SCF	ECCSD	SRCCSD	Expt or correlation
α_{zz}	8.52	9.15	9.66[a]	9.64[b] 9.59[c] 9.91±0.02[e]
α_{xx}	9.19	9.84	10.04[a]	9.81[b] 9.93[c] 10.31±0.08[e]
α_{yy}	7.85	9.14	9.46[a]	9.59[b] 9.34[c] 9.5±0.08[e]
A_{xzx}	6.27(6.71)	6.66	6.80[a]	6.722[d]
A_{yzy}	1.40(1.69)	1.48	1.62[a]	1.786[d]
A_{zxx}	1.62(2.08)	1.77	1.74[a]	2.54[f] 4.07[d]
A_{zzz}	1.68(1.90)	1.81	1.91[a]	2.194[d] 2.44[f]
Θ_{xx}	1.89	1.90	1.90[a]	1.912[c] 1.96±0.2[g]
Θ_{yy}	-1.79	-1.80	-1.81[a]	-1.804[c] -1.86±0.2[g]
Θ_{zz}	-0.097	-0.093	-0.092[a]	-0.108[c] -0.10±0.2[g]

a Dalton CCSD results; b See Ref. [19]; c See Ref. [48]; d CISD see Ref. [47]
e See Ref. [49]; f MCSCF see Ref. [45]; g See Ref. [50].

Table 3.6 Properties of water in a.u. using Sadlej basis.

Basis	Property	SCF	ECCSD	SRCCSD
cc-pVDZ	α_{zz}	3.06	3.14	3.20[a]
	α_{xx}	6.93	7.00	7.07[a]
	α_{yy}	5.11	5.23	5.28[a]
	A_{xxy}	-7.53	-7.63	-7.73[b]
	A_{yxx}	-2.69	-3.06	-3.09[b]
	A_{yyy}	-0.963	-0.944	-0.963[b]
	A_{zyz}	-1.07	-1.10	-1.12[b]
	Θ_{xx}	1.65	1.54	1..57[b]
	Θ_{yy}	-1.58	-1.59	-1.50[a]
	Θ_{zz}	-0.075	-0.073	-0.073[a]
aug-cc-pVDZ	α_{zz}	7.33	8.34	8.73[a]
	α_{xx}	9.04	9.58	9.89[a]
	α_{yy}	8.09	8.79	9.00[a]
	A_{xxy}	-6.85	-7.35	-7.54[b]
	A_{yxx}	-2.30	-2.42	-2.54[b]
	A_{yyy}	-1.72	-2.08	-2.22[b]
	A_{zyz}	-1.56	-2.24	-2.42[b]
	Θ_{xx}	1.88	1.72	1.89[a]
	Θ_{yy}	-1.80	-1.96	-1.806[a]
	Θ_{zz}	-0.090	-0.088	-0.087[a]

[a] Dalton CCSD results; [b] Finite field results

3.3.5 Ammonia

Ammonia is studied in cc-pVDZ as well as aug-cc-pVDZ basis set with the geometry of the molecule as 1.012 Å as N–H bond lengths and H–N–H bond angle 106.7. We report the three components of the dipole–quadrupole polarizability. It can be seen from the results in Table 3.7, that with augmentation of the basis dipole polarizabilities are enhanced whereas dipole–quadrupole polarizability values are reduced except for the component. ECCSD and SRCCSD are in good agreement with each other for most of the properties except for the A_{zzz} component of the dipole–quadrupole polarizability. The SRCCSD value of A_{zzz} component is obtained using finite difference method whereas our value is obtained from analytic response approach. Due to the lone pair on the nitrogen, relaxation is large when field is applied along the z-direction. In fact relaxation cancels the correlation and we get close to SCF value in both the basis sets. To confirm our point we also carried out finite field calculation using ECCSD functional. These values are reported in parenthesis. It can be seen that out finite field value agrees well with the SRCCSD confirming that the difference is due to the relaxation.

Table 3.7 Properties of ammonia in a.u.

Basis	Property	SCF	ECCSD	SRCCSD
cc-pVDZ	α_{zz}	7.57	7.61	7.73[a]
	α_{xx}	8.20	8.21	8.31[a]
	α_{yy}	9.36	9.31	9.40[a]
	A_{xyy}	-6.67	-6.03	-6.67[b]
	A_{yxy}	-9.61	-10.80	-9.59[b]
	A_{zzz}	4.01	6.77(4.01)	4.01[b]
	Θ_{zz}	-0.72	-0.74	-0.82[a]
	α_{zz}	12.81	13.89	14.39[a]
	α_{xx}	12.71	13.59	14.13[a]
	α_{yy}	12.51	13.02	13.36[a]
	A_{xyy}	-4.82	-3.54	-4.87[b]
	A_{yxy}	-7.45	-9.08	-7.40[b]
	A_{zzz}	4.11	7.10(4.56)	4.00[b]
	Θ_{zz}	-0.876	-0.884	-0.828[a]

[a] *Dalton CCSD results;* [b] *Finite field results*

3.4. Conclusion

In this chapter we report dipole–quadrupole polarizability of methane, tetrafluoromethane, water, ammonia, carbon monoxide and hydrogen fluoride. Quadrupole moment of acetylene, difluoroacetylene, water and ammonia are calculated. Dipole polarizabilities for all the molecules are reported. We have used ECCSD method in the chapter. In the present chapter we have included all the double linked terms that appear in the functional within CCSD approximation. To compare the difference between the previous cubic truncation and current approximation we have studied the carbon monoxide and hydrogen fluoride molecule at different bond distances. Our results indicates the importance of the current approximation at the stretched geometries.

We observe that with augmentation of the basis set dipole polarizabilities are enhanced, whereas dipole–quadrupole polarizabilities are reduced in general. For methane the A_{xyz} component is reduced by 35%whereas for tetrafluoromethane A_{xyz} component is reduced by 15%with the augmentation of the basis set. In case of water the A_{yyy} and A_{zyz} components are almost doubled. The two other components, i.e. A_{xxy} and A_{yxx} are marginally reduced. In case of ammonia the A_{zzz} component is enhanced marginally. However, two other components are reduced with augmentation of the basis set. In case of the A_{zzz} component of ammonia our analytic ECCSD value differs largely with the finite field SRCCSD value in both the basis sets. The difference is due to relaxation. To make sure that the difference is indeed due to relaxation we also report finite field ECCSD value for A_{zzz} component. We found that our finite field ECCSD value is in good agreement with SRCCSD. It is interesting to note that, due to presence of lone pair on nitrogen, when field is applied along z direction the relaxation effect cancels correlation effect.

The quadrupole moment values for acetylene and difluoroacetylene are in good agreement with the other theoretical values in the literature. The sign of the quadrupole moment is reversed when H atom is replaced by F atom. In general our values are in good agreement with other theoretical and SRCCSD values.

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Chapter 4

Extended Coupled Cluster Method for Potential Energy Surface: a Decoupled Approach

Extended Coupled Cluster (ECC) method has been implemented extensively for the calculation of molecular properties. In this paper we report the potential energy surface (PES) study using coupled ECC and a decoupled approximation of ECC. HF, N_2 and C_2 are studied as test systems. N_2 and C_2 being doubly and triply bonded, are considered to be interesting systems for PES study. We compare our results with Full CI (FCI) results wherever available. Decoupled approach within ECC framework shows good convergence for all the molecules.

4.1 Introduction

Study of potential energy surface (PES) provides a key to understand various chemical reactions [1], kinetics, dynamics [2-4] and spectroscopic properties. In recent years, there have been a lot of studies on PES [2-5]. Hartree Fock [6-7] is used as a zeroth order approximation for the correlated calculations. Among the correlated methods, single reference coupled cluster (SRCC) method [8-12] has been accepted as the most accurate method even in its approximate form. SRCC has been extensively used for the calculation of energy [13-15] and energy derivatives [16-21] as well as for potential energy surface calculations. Application of SRCC for the PES calculations at the bond breaking region is one of the most challenging problems. Though SRCC is suitable at the ground state geometry, it fails completely at the dissociation limit in particular when RHF does not dissociate correctly, where the non-dynamical correlation dominates [22-24]. To overcome this problem higher order terms like triples and quadruples are included [25] or multi reference methods are used [26,27]. Various studies have been performed for the calculation of PES using variational coupled cluster method [28-31]. Being variational it has upper bound in energy and does not collapse like standard SRCC method. Expectation values coupled cluster (XCC) [32], unitary coupled cluster (UCC) [33], Extended coupled cluster (ECC) [34-37], improved coupled cluster (ICC) [30] and quadratic coupled cluster (QCC) [31] are some of the variants of the variational coupled cluster approach. However, all the variational methods suffer from the problem of non-terminating series and needs to be truncated for practical application. Various truncation schemes are available in the literature. Energy functional in variational CC theory includes connected diagrams, however, when differentiated leads to disconnected diagrams giving loss of size extensivity. ECC functional due to the double linked nature always maintains linked diagrams even after differentiation and therefore the size extensivity is maintained [37]. However, this has double the number of amplitudes and hence twice the no. of equations to be solved. Decoupled approximation has been proposed to solve this problem. Decoupled approximation was implemented for electric properties at the equilibrium geometry and is successfully tested for closed shell systems [38].

Last decade has witnessed a wide variety of study on potential energy surfaces. The incorrect convergence of RHF based studies makes it challenging for any SRCC method to study PESs. Musial *et. al.* [25] has shown that the ΛCCSD(TQ$_f$) approximation, based on Λ^2CCSD(TQ$_f$) method, gives improvement in the PESs due to the inclusion of the connected factorized quadruples. Knowles and co-workers [30,31] used different approximations of the variational coupled cluster method for the study of potential energy surfaces. Piecuch *et. al.* [26] used renormalized non-iterative coupled cluster method for the study of PESs. Current letter emphasizes on the study of extended coupled cluster (ECC) method along with promising decoupled approximation for the potential energy surface. We have studied close shell molecules like HF, N_2 and C_2 in bond breaking region. All the three systems are very well studied in the literature before, due to the challenges they possess.

Paper is organized in the following manner. In section II we briefly discuss the Extended coupled cluster (ECC) method along with the decoupled approximation. Results and discussion on them is done in section III. Conclusions on the results are presented in Section IV.

4.2 Theory

We briefly discuss the Extended Coupled Cluster (ECC) functional, that we have used for PES study. The ECC functional uses different ket and bra vectors.

$$E = \left\langle \Psi' \middle| H \middle| \Psi \right\rangle \tag{4.1}$$

$$\left| \boldsymbol{\Psi} \right\rangle = e^{T} \left| \boldsymbol{\Phi} \right\rangle \tag{4.2}$$

$$\left\langle \boldsymbol{\Psi}' \right| = \left\langle \boldsymbol{\Phi} \right| e^{\boldsymbol{\Sigma}} e^{-T} \tag{4.3}$$

Here Σ is a hole particle de-excitation operator while T is hole particle excitation operator.

They can be defined as,

$$T = \sum_i t_i C_i^\dagger \tag{4.4}$$

$$\boldsymbol{\Sigma} = \sum_i \sigma_i C_i \tag{4.5}$$

Here Ψ' and Ψ are bi-orthogonal to each other and they are differently parameterized. Arponen [34] and Bishop [35] first time proposed the functional for calculating energy and is popularly known as ECC.

After performing double similarity transformation the functional is written in the following form

$$E = \left\langle \Phi_o \middle| e^{\Sigma} (He^T)_L \middle| \Phi_o \right\rangle_{DL} \tag{4.6}$$

DL implies that the right operator must be connected to the Hamiltonian H. The subscript DL (double linked) signifies the left vector Σ is either connected to the Hamiltonian H or to two different T operators. Thus, DL conforms that the series is naturally terminating and thus gives size extensive energy and properties [33]. Double linking also ensures that we have only connected diagrams.

The form of the functional used in this letter is as follows,

$$\begin{aligned}
E = \langle \boldsymbol{\Phi} | & vt_2 + \sigma_2 v + \sigma_1 vt_1 + \sigma_2 vt_2 + \sigma_1 vt_2 + \sigma_2 vt_1 + \\
& \sigma_1 ft_1 + \sigma_2 ft_2 + \frac{1}{2}\sigma_1\sigma_1 v + \frac{1}{2} vt_1t_1 + \frac{1}{2}\sigma_1 vt_1t_1 + \frac{1}{2}\sigma_2 vt_1t_1 \\
& \frac{1}{2}\sigma_1\sigma_1 vt_1 + \sigma_1\sigma_2 vt_2 + \sigma_1 vt_2t_1 + \sigma_2 vt_2t_1 + \frac{1}{2}\sigma_2 vt_2t_2 + \\
& \frac{1}{2!}\sigma_2 vt_2t_1^2 + \frac{1}{3!}\sigma_2 vt_1^3 + \frac{1}{4!}\sigma_2 vt_1^4 + \frac{1}{3!}\sigma_1^3 vt_2 + \frac{1}{2!}\sigma_2 vt_1t_1 | \boldsymbol{\Phi} \rangle
\end{aligned} \tag{4.7}$$

It can be seen that, the contribution of the right operator is taken full within CCSD approximation, also the terms we use are double linked within CCSD model. They include $vt_1^4, vt_1^3, vt_2t_1^2$ etc. in doubles amplitude equation and vt_1^3 in singles amplitude equation. While left operator includes all the conjugate double linked terms i.e. $\sigma_2 vt_1^2$, $\sigma_1^3 v$ in σ_2 equation and $\sigma_2 vt_1t_2$, $\sigma_2 vt_1^2$, $\sigma_2 vt_1^3$ in σ_1 amplitude equation, within CCSD approximation. The initial implementation was based on the cubic truncation of the left and right vector. Thus, the extra terms compared to the cubic approximation are $\Sigma_2\, VT_2{T_1}^2$, $\Sigma_2 V{T_1}^3$, $\Sigma_2 V{T_1}^4$, ${\Sigma_1}^3 VT_2$. However, we have not included terms like $\sigma_2^2 vt_2^2$ and some other terms like this.

The amplitude equations are obtained by differentiating energy expression with respect to cluster amplitudes i.e.

$$\frac{\partial E}{\partial t} = 0 \tag{4.8a}$$

$$\frac{\partial E}{\partial \sigma} = 0 \tag{4.8b}$$

Differentiation with respect to t amplitudes gives equation for σ amplitudes, while differentiation with respect to σ amplitudes gives equation for t amplitudes.

Equations for $\sigma_2^{(0)}$ and $\sigma_1^{(0)}$ amplitudes are given below

$$\begin{aligned}\frac{\partial E}{\partial \tilde{\sigma}_2^{(0)}} &= \left\langle \boldsymbol{\Phi}_{ab}^{pq} \right| \hat{V} + \hat{V}\sigma_1^{(0)} + (\hat{\mathrm{F}} + \hat{V})\sigma_2^{(0)} + \frac{1}{2!}\hat{V}\sigma_1^{(0)}\sigma_1^{(0)} \\ &+ \hat{V}\sigma_1^{(0)}\sigma_2^{(0)} + \frac{1}{2!}\hat{V}\sigma_2^{(0)}\sigma_2^{(0)} + \tilde{\sigma}_1^{(0)}\hat{V}\sigma_2^{(0)} + \frac{1}{2!}\hat{V}\sigma_2^{(0)}\left(\sigma_1^{(0)}\right)^2 \\ &+ \frac{1}{3!}\hat{V}\left(\sigma_1^{(0)}\right)^3 + \frac{1}{4!}\hat{V}\left(\sigma_1^{(0)}\right)^4 \left| \boldsymbol{\Phi}_0 \right\rangle = 0\end{aligned} \tag{4.9a}$$

$$\begin{aligned}\frac{\partial E}{\partial \tilde{\sigma}_1^{(0)}} &= \left\langle \boldsymbol{\Phi}_a^p \right| \tilde{\sigma}_1^{(0)}\hat{V} + (\hat{\mathrm{F}}+\hat{V})\sigma_1^{(0)} + \hat{V}\sigma_2^{(0)} + \frac{1}{2!}\hat{V}\sigma_1^{(0)}\sigma_1^{(0)} \\ &+\hat{V}\sigma_1^{(0)}\sigma_2^{(0)} + \tilde{\sigma}_1^{(0)}\hat{V}\sigma_1^{(0)} + \tilde{\sigma}_2^{(0)}\hat{V}\sigma_2^{(0)} + \frac{1}{2!}\left(\tilde{\sigma}_1^{(0)}\right)^{(2)}\hat{V}\sigma_2^{(0)}\left|\boldsymbol{\Phi}_0\right\rangle = 0\end{aligned} \tag{4.9b}$$

In similar way, equations for $\tilde{\sigma}_2^{(0)}$ and $\tilde{\sigma}_1^{(0)}$ are given as

$$\begin{aligned}\frac{\partial E}{\partial \sigma_2^{(0)}} &= \left\langle \boldsymbol{\Phi}_0 \right| \hat{V} + \tilde{\sigma}_1^{(0)}\hat{V} + \tilde{\sigma}_2^{(0)}(\hat{\mathrm{F}}+\hat{V}) + \frac{1}{2!}\tilde{\sigma}_1^{(0)}\tilde{\sigma}_1^{(0)}\hat{V} \\ &+\tilde{\sigma}_1^{(0)}\tilde{\sigma}_2^{(0)}\hat{V} + \tilde{\sigma}_1^{(0)}\hat{V}\sigma_1^{(0)} + \tilde{\sigma}_2^{(0)}\hat{V}\sigma_1^{(0)} + \tilde{\sigma}_2^{(0)}\hat{V}\sigma_2^{(0)} \\ &+\frac{1}{2!}\tilde{\sigma}_2^{(0)}\hat{V}\left(\sigma_1^{(0)}\right)^2 + \frac{1}{3!}\left(\tilde{\sigma}_1^{(0)}\right)^3\hat{V}\left|\boldsymbol{\Phi}_{ab}^{pq}\right\rangle = 0\end{aligned} \tag{4.10a}$$

$$\begin{aligned}\frac{\partial E}{\partial \sigma_1^{(0)}} &= \left\langle \boldsymbol{\Phi}_0 \right| \hat{V}\sigma_1^{(0)} + \tilde{\sigma}_1^{(0)}(\hat{\mathrm{F}}+\hat{V}) + \tilde{\sigma}_2^{(0)}\hat{V} + \frac{1}{2!}\tilde{\sigma}_1^{(0)}\tilde{\sigma}_1^{(0)}\hat{V} \\ &+\hat{V}\sigma_1^{(0)}\sigma_2^{(0)} + \tilde{\sigma}_1^{(0)}\hat{V}\sigma_1^{(0)} + \tilde{\sigma}_2^{(0)}\hat{V}\sigma_2^{(0)} + \tilde{\sigma}_2^{(0)}\hat{V}\sigma_1^{(0)} + \tilde{\sigma}_1^{(0)}\hat{V}\sigma_2^{(0)} \\ &\tilde{\sigma}_2^{(0)}\hat{V}\sigma_2^{(0)}\sigma_1^{(0)} + \frac{1}{2!}\tilde{\sigma}_2^{(0)}\hat{V}\left(\sigma_1^{(0)}\right)^{(2)} + \frac{1}{3!}\tilde{\sigma}_2^{(0)}\hat{V}\left(\sigma_1^{(0)}\right)^{(3)}\left|\boldsymbol{\Phi}_a^p\right\rangle = 0\end{aligned} \tag{4.10b}$$

For cluster amplitudes (4.9a) and (4.9b) along with (4.10a), (4.10b), we solve them iteratively to get the accurate energy. It can be seen that ECC method contains double the number of terms and hence amplitude equations compared to the SRCC approximation. This at times gives problem in convergence. Decoupled approximation is used as an alternative to eliminate this problem. The discussion on it is done in next section.

4.2.1 Decoupled Scheme:

The ECC functional behaves very well at equilibrium and stretched geometries around equilibrium. However, near bond breaking region ECCSD possess problem of convergence. To overcome this problem we have used a decoupled scheme for the study of PES.

Current decoupled scheme separates the left and right cluster operators. Equation (4.8b) gives the amplitudes within singles and doubles approximations and they are very similar to non- variational coupled cluster (NVCC) equation. Thus, initially we determine the t amplitudes eliminating σ amplitudes. Once t amplitudes are known, we treat them as constant. We then solve the equation for σ amplitudes i.e. equation (4.8a). Then we come back to the t amplitude equation. This time we consider all the terms including σ amplitudes, however, σ amplitudes are treated as constant. Again, we go back to the σ amplitude equation. Thus, in the decoupled approximation we have both the amplitudes but we treat the other amplitude as a constant and hence every time only half the numbers of cluster amplitudes are included. Using these left and right cluster amplitudes we evaluate the potential energy surface (PES) for singly and multiply bonded systems. The number of cluster amplitudes are reduced, in the decoupled scheme as compared to ECC, though the numbers of equations are same. At the equilibrium geometry, coupled and decoupled scheme take almost same time. However, at stretched geometries decoupled scheme takes more computer time compared to coupled scheme. Despite this the decoupled scheme is preferred due to convergence problem that we face for the coupled scheme.

4.3 Results and Discussion

We present the study of potential energy surfaces for HF, C_2 and N_2 molecules using ECC functional. Here we report the results obtained for these systems with ECCSD method where equations are solved in a coupled as well as in a decoupled manner. All the three systems are very well studied for the PES. We have chosen the basis sets such that we can compare our results with the existing literature results. We compare our results with FCI method wherever possible. Hydrogen Fluoride molecule has been studied in DZ (Dunning) [39] basis set. C_2 molecule has gained a vital importance due to its role in combustion reaction and also due to its multi-reference character at equilibrium geometry. Hence the system becomes an interesting candidate for the study. We study the PES for C_2 in 6-31 G* [40, 41] bases set and compare our results with FCI results reported in the literature. N_2 being strongly correlated system proves to be a good example to study PES. We have studied N_2 in DZP [42] basis set and for comparison the CCSD (T) method has been used. To start with the calculations we have considered RHF determinant. CCSD (T) as well as FCI results are obtained using GAMESS [43] package. Results for PES are shown in figures from 1-3.

4.3.1 Hydrogen Fluoride:

PES for Hydrogen Fluoride molecule has been studied very well with various methods and is documented in literature [25, 30, 31, and 44]. All electrons are correlated in our calculations and we compare our results with FCI values. Energies are calculated for bond lengths ranging from 1.2996 (0.75 R_e) to 6.238 (3.6R_e) Bohr. The equilibrium (R_e) bond length is 1.7328 Bohr. Figure 1 represents the potential energy curve for HF. The potential energy curve for HF can be divided into two parts. Part one consists from 0.75R_e to 1.5 R_e where the RHF configuration is a good approximation for the exact wave function. The electronic configuration at the equilibrium geometry is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^2(2\pi)^2 \,|\, (4\sigma)^0 .....$$

Around equilibrium only dynamic correlation is dominant. As we go towards stretched geometry static correlation becomes crucial. At 1.5R_e onwards the RHF electronic configuration changes to

$$(1\sigma)^2(2\sigma)^2(1\pi)^2(2\pi)^2(3\sigma)^2 \,|\, (4\sigma)^0$$

The configuration which involves bi-excitation $(3\sigma)^2 \to (4\sigma)^2$ becomes equally important as the ground state configuration. This makes it difficult for the convergence of the ECC equation in particular when solved in a coupled manner. As a result we are not able to converge the ECC equation beyond 2.75 R_e. At 3.6 R_e FCI expansion coefficient for the above bi-excitation is 0.6163 compared to the ground state coefficient of 0.6474. This indicates the importance of static correlation at 3.6 R_e.

From the curves in figure 1 we can see that with the decoupled approach curve performs very well and shows the same trend like FCI i.e. reference curve. The difference between FCI and ECCSD decoupled approach is very small i.e. 0.005 a.u. From 3 Bohr onwards coupled ECCSD starts to differ with the FCI. Our results obtained using decoupled approach represents the curve is very close to the FCI and thus this scheme is significantly better than coupled ECCSD in terms of faster the convergence.

HF molecule DZ (Dunning) basis set

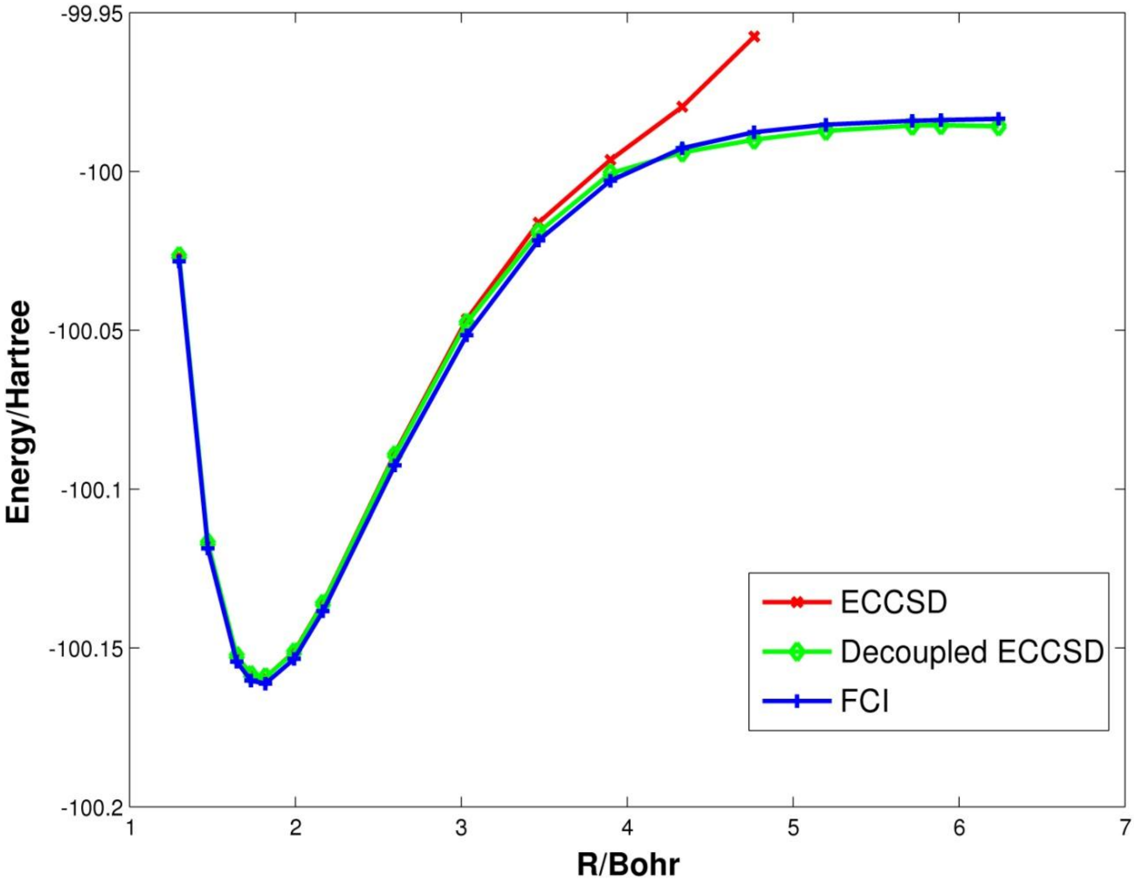

Figure 4.1: Potential Energy Curve for HF molecule

4.3.2 Nitrogen

The electronic configuration of N_2 molecule is given as,

$$(1\sigma)^2\ \ (2\sigma)^2\ (3\sigma)^2\ (4\sigma)^2\ (5\sigma)^2\ (1\pi)^2\ (2\pi)^2\ |\ (6\sigma)^0$$

We have studied N_2 molecule in DZP (Dunning) basis. However, there are no FCI results are available in this basis, in the literature.

Since the system is strongly correlated, the static correlation plays dominant role starting from equilibrium geometry itself. Also N_2 being triply bonded is an interesting system for the PES study. N_2 is studied by Piecuch and co-workers in STO-3G basis using ECCSD method. Although, in their study functional is not double linked and also many higher order terms like $\sigma_2^2 v t_2^2, \sigma_1 \sigma_2 v t_2^2$, etc. are included, which are missing in our study. All electrons are correlated in our study. PES is calculated for bond lengths ranging from 1.8 to 4.25 Bohr. The equilibrium bond length is taken as 2.07 Bohr. It is known that for N_2 higher excited amplitudes i.e. T_3 and T_4 play an important role [25, 29].

Figure 2 gives the PES calculated with coupled and decoupled ECC method along with coupled cluster singles and doubles (CCSD) and coupled cluster singles and doubles using partial triples CCSD (T). There has been a wide study over N_2 molecule using CC approximations. We have reported the curve using CCSD (T) for comparison accompanied by CCSD. From figure 2 we can see that the difference between the CCSD and CCSD (T) is about 0.05 a.u. The difference increases rapidly after 3 Bohr showing the importance of higher excitation amplitudes i.e. T_3. Inclusion of T_4 and higher excitations furthermore with a variational approach may help in improving the results towards FCI. However, CCSD as well as CCSD (T) fall off after 3.5 Bohr. The strong triple bond breaking might be complicated due to effect of static correlation. Decoupled scheme makes the evaluation of static correlation feasible.

N_2 molecule DZP basis set

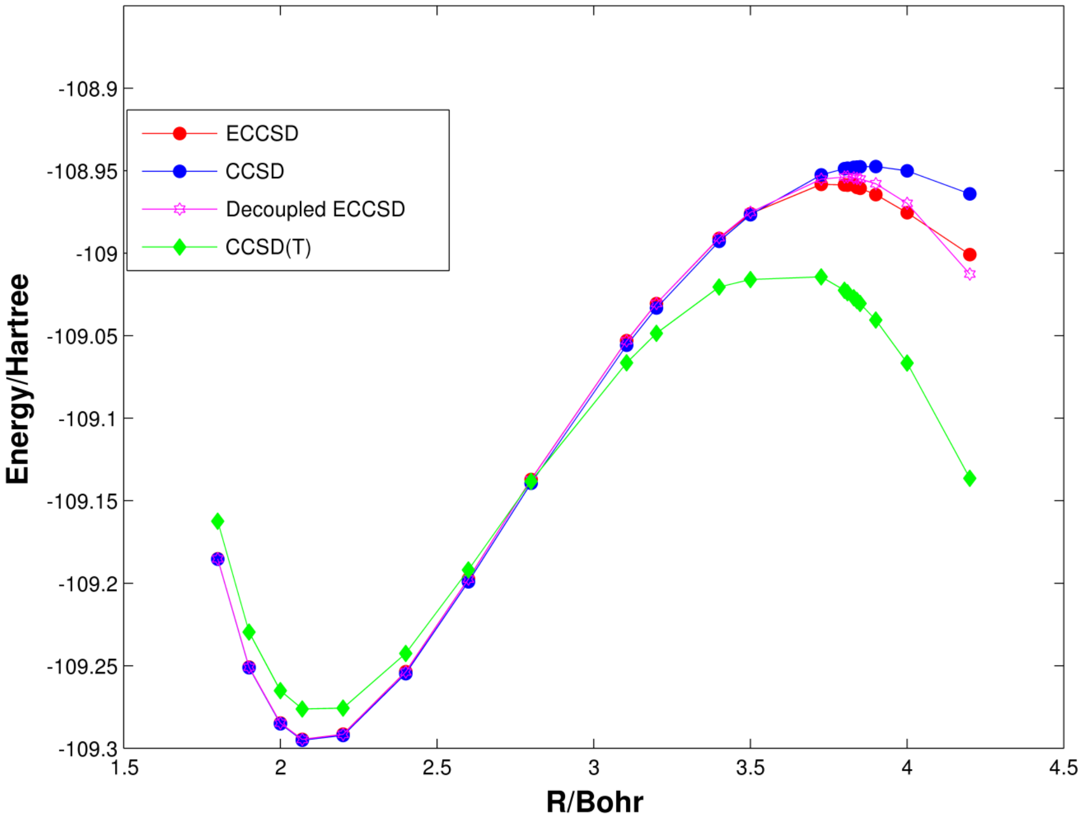

Figure 4.2: Potential Energy Curve for N_2 molecule

4.3.3 Carbon Dimer

The electronic configuration of C_2 is given as,

$$(1\sigma)^2\ (2\sigma)^2\ (3\sigma)^2\ (4\sigma)^2\ (5\sigma)^2\ (1\pi)^2\ |\ (6\sigma)^0$$

C_2 is an interesting system to study because of the near degeneracy of $3\pi_u$ state with the ground state, along with a strong multireference character. C_2 has been tested by various correlated methods due to its quasi degenerate nature [25, 27, 30, 31, 45, 46]. We have chosen 6-31 G* basis set for our study due to the availability of results in the literature for comparison [45, 46]. The equilibrium bond length is 2.377 Bohr (1.243 Å), taken from experimental geometry. The bond is stretched until 5.67 Bohr (3 Å). We compare our results with FCI [45] and completely renormalized [CR-CCSD (TQ)] coupled cluster method with triple and quadruples excitation studied by Sherrill and co-workers [46]. CR-CCSD (TQ) method also overestimates energy compared to full CI, however, it is lower compared to ECCSD.

Figure 3 gives all the details of curves using different methods. It can be seen that full ECCSD and decoupled ECCSD both the methods perform similar for C_2 molecule. Compared to FCI, both ECCSD and decoupled ECCSD are on the higher side as expected. However, qualitative trend is obtained correctly. Thus, inclusion of the non-iterative triples and quadruples should improve the results for ECC method too. However, they are computationally very expensive. Within CCSD approximation ECC being variational does not fall off and gives qualitatively correct behaviour.

C_2 molecule in 6-31G* basis set

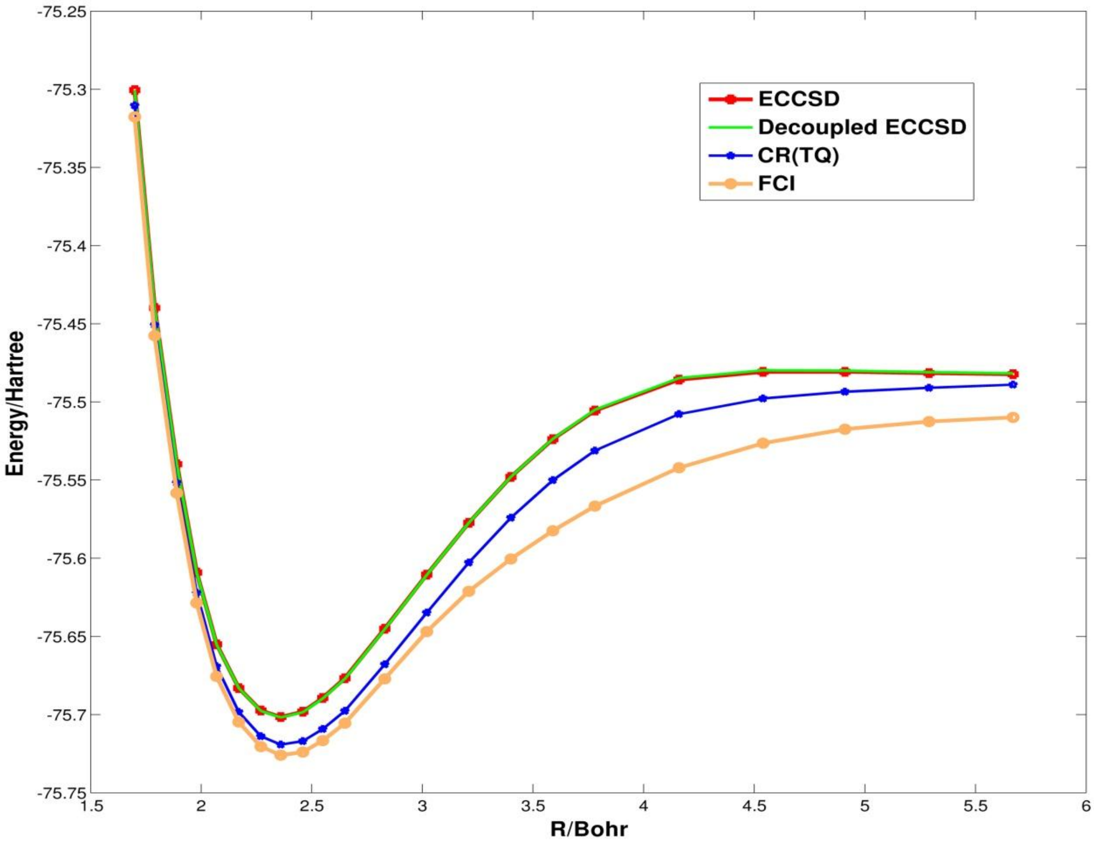

Figure 4.3: Potential Energy Curve for C_2 molecule

4.4 Conclusion:

For efficient and accurate calculation of potential energy surfaces of HF, N_2 and C_2 molecules we have used ECC method. ECC equations were solved in a coupled as well as decoupled manner. We present results using both the methods. We have compared the results with FCI wherever available. Though both coupled and decoupled ECC method contain same number of terms, the decoupled scheme proves a better option near bond breaking region. Since coupled ECC contains 2n number of equations to be solved at stretched geometries it is difficult to converge. However the decoupled scheme takes advantage of considering half the number of equation at a time, thereby reducing the complications in computational calculations. For all the molecules the decoupled scheme behaves very well.

For N_2 molecule we have compared our results with CCSD(T) method. Decoupled scheme provides better results for all the systems at the dissociation limit. The decoupled ECC method takes care of static correlation to some extent. However, in cases where static correlation dominates even in the ground state it may fail to take care of it i.e. Cr_2. In such cases quadratic terms along with the higher body excitation term like triples, quadruples may help. However, use of multi-reference based methods will be more effective.

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Chapter 5

Formulation of analytic gradients using extended coupled cluster method

We explain the formulation of the analytic gradient using ECC approach. The coupled perturbed Hartree-Fock equation is used (CPHF) for the derivative calculation of the coefficient matrix and Fock matrix. ECC being fully variational, we do not require derivative cluster amplitudes for calculation of gradients. However, to obtain the relaxed density, we need to solve Z-vector equation. One and Two particle density matrices are calculated and are back transformed to obtain in atomic basis. These densities in AO basis are then contracted with derivative Hamiltonian to acquire the gradient of energy. The final goal is geometry optimization using the gradient obtained by ECC.

5.1 Introduction

Obtaining molecular structures by quantum chemical methods is becoming more and more widespread phenomena[1-2] . The knowledge of analytic gradients is useful in the determination and characterization of equilibrium geometries, transition states, and reaction paths of molecular potential energy surfaces. Perturbations like electric or magnetic along with the geometric perturbation are important. These derivatives can be linked to quantities which can be measured experimentally. Structures obtained using ab initio techniques for small molecular systems rival in accuracy with those obtained from experiment. Implementation of analytic calculation of energy derivatives with respect to nuclear coordinates has revolutionized the use of quantum chemistry techniques for routine calculations of molecular structures and properties [3-5]. In most cases cost of calculation of first derivatives is comparable to the calculation of energy and has helped in increasing popularity of quantum chemistry methods. It is possible to calculate energy derivatives using finite field [6-7]. However, the accuracy of the derivative is lost. Secondly, for derivative with respect to nuclear coordinates, which has 3N-6 degrees of freedom which complicates the calculation and as size of the system increases number of parameters increase and it becomes difficult/expensive to use numerical methods. Use of analytical methods is more useful or a wise choice in case where perturbation parameters are many.

The analytical gradient method was first implemented by Pulay *et. al.* [6,8] He calculated analytic gradient for Hartree-Fock (HF) method [8,9] to calculate the equilibrium geometries. However, calculation of derivatives of one-electron and two-electron integrals over AO basis was the main hurdle. Later Pople and co-workers implemented analytic hessian for Hartree Fock method [10]. The success of their method involved the efficient implementation to solve coupled perturbed HF (CPHF) equations. Initial implementation of analytic gradient in the context of Møller- Plessete (MP2) perturbation theory, which gives electron correlation, is done by Almlöf [11] and Pople and co-workers [12]. Here too efficient solution of CPHF equations [13-15]was important for the success of the method . Hatree Fock [16,17] is variationally optimized with respect to the coefficient, however, correlated methods are not. Hence, we need method called Z-vector[18] to eliminate this problem.

The analytic calculation of energy derivative methods beyond Hartree Fock were important due to the fact that they introduce electron correlation which plays important role. Among the methods beyond HF are Configuration Interaction (CI) [19,20], perturbation theory (MBPT) [21-23] and coupled cluster method (CC) [24-29]. The main advantage of the perturbation theory is it gives size-extensive properties at each level of truncation. However, MP theory has its disadvantage, since it is not variational in nature does not promise that the energy obtained is always upper bound to the ground state energy. Configuration Interaction method (CI) loses its size-extensivity when truncated i.e. CID, CISD, etc. Hence, one has to correct the CI description using some empirical correction terms. Pople, Head-Gorden and Raghavachari invented [30] a new modified method based on HF wave function for calculating correlation energies in reference with CI method. They suggested to add new terms to CI equations, those are quadratic in CI coefficients. This leads to the correction of size-extensivity error present in truncated CI. This was termed as QCI and it was established as the promising way of calculating electron correlation. Jørgensen and Simons [31] formulated analytical MP3 and CCD gradient of energy. First implementation of analytic MP3 gradients was done by Bartlett and co-workers[32]. However the computer program was not efficient and required full transformation of two electron integrals from AO to MO basis and was the most costliest and unnecessary step in the calculations. Proper implementation of MP3 analytic gradients was represented by Gauss and Cramer in 1987[33]. Similar type of work was carried out by Bartlett and co-workers. Handy et. al. [34] formulated and implemented analytic gradient technique in the context of unrestricted HF (UHF) method. The analytical MP4 gradient theory was formulated by Bartlett *et. al*. [35-36] while the implementation of the method was done by Gauss.

Single reference coupled cluster (SRCC) [24-29] methods are widely applied to different systems for accurate prediction of electron correlation. The major advantage of the method over other methods like CI is, it gives size-extensive results even in its approximate form for energy calculation. Handy and Scheafer showed that the Z-vector [18] technique can be used for elimination of amplitude derivatives, thus the equation can become independent of perturbation dependent terms. Adamowicz, Laiding and Bartlett [36] formulated analytical coupled cluster singles and doubles (CCSD) gradient using Z-vector method. The introduction of Z vector within CC gradient has made method very powerful and successful.

The variational or stationary methods play important role in determining the molecular properties accurately since they follow generalized Hellmann-Feynman theorem (2n+1). Expectation value CC (XCC) [37-40], unitary CC (UCC) [41-44] and extended CC (ECC) [45-47] are the functional used in the variational approach. Expectation value (XCC) is used for the calculation of analytic gradient by Bartlett and co-workers [48] . They studied the first and higher order properties through truncation of XCC at the order of n i.e. XCC(n) to evaluate potential energy surface as well as to predict vibrational spectra. However, XCC when truncated has disconnected diagrams. This leads to loss of size extensivity in the property calculations. UCC functional was mostly tried for the energy calculations. Arponen and Bishop suggested a bi-orthogonal functional named as extended coupled cluster (ECC). Pal and co-workers have studied this functional extensively to obtain electric as well as magnetic properties of molecules [49- 52]. The functional is double linked in nature which makes it naturally terminating series. However, termination is at high order and for practical application need to be truncated. Double linking also ensures that energy and energy derivatives are always linked. Being variational it also satisfies Hellmann Feynmann theorem. Which makes this functional ideal candidate for the energy derivatives, in particular higher order derivatives.

In the present chapter, we have done the formulation of gradient using ECC approach. We outline the procedure for the gradient calculation using ECC functional. Our final aim is to perform geometry optimization using calculated gradient. The chapter consists of section 5.2 that will give the formulation of gradient using ECC density. The geometry optimization is represented by a flowchart, that will give the detail idea about the geometry optimization procedure. The gradient calculation with ECCSD density is in progress. The codes are under testing condintion.

5.2 Theory

5.2.1 Extended Coupled Cluster Approach

The bi-orthogonal functional was developed by Arponen and Bishop to calculate energy [45,46]. This is termed as Extended coupled cluster approach (ECC) and contains two different set of parameters represented by bra and ket.

$$\begin{aligned}\left\langle \hat{H} \right\rangle &= \left\langle \Psi' \middle| \hat{H} \middle| \Psi \right\rangle \\ \left\langle \hat{H} \right\rangle &= \left\langle \Phi_0 \middle| \left(1+\Omega\right) e^{-T} H e^{T} \middle| \Phi_0 \right\rangle\end{aligned} \tag{5.1}$$

In equation (5.1) $\left\langle \Psi' \right|$ and $\left| \Psi \right\rangle$ are the two set of parameters, which are parameterized differently. T is a hole-particle excitation operator while Ω is a linear operator and includes hole-particle de-excitation operator, the operator resembles with the T^{+} operator. Φ_0 is the Hartree-Fock determinant i.e. the reference function. Thus we can write the equations as

$$\begin{aligned}\left\langle \Psi' \middle| \Psi \right\rangle &= 1 \\ \left\langle \Phi_0 \middle| \Psi \right\rangle &= 1\end{aligned} \tag{5.2}$$

Performing double similarity transformation on the functional we obtain

$$\begin{aligned}\left\langle E \right\rangle &= \left\langle \Phi_0 \middle| e^{\Sigma} e^{-T} H e^{T} e^{-\Sigma} \middle| \Phi_0 \right\rangle_{DL} \\ \left\langle E \right\rangle &= \left\langle \Phi_0 \middle| e^{\Sigma} (He^{T})_L \middle| \Phi_0 \right\rangle_{DL}\end{aligned} \tag{5.3}$$

In equation (5.3), the subscript *L* represents the direct linking of *T*-amplitudes with Hamiltonian *H*. The subscript *DL* indicates the double linking of the functional i.e. the left operator Σ either has to be connected to Hamiltonian *H* or should be connected to minimum two different *T* amplitudes. The double linking ensures the connectedness in the energy as well as amplitude terms. Also the energy derivatives along with the cluster amplitude derivatives are connected at any order of truncation. The advantage with the ECC anasatz is the series is naturally terminated. However, for practical systems the truncation of the series occurs at quite higher order and hence for practical application we need to truncate the series.

To calculate the ground state cluster amplitudes for T and Σ variationally, energy is made stationary with respect to t and σ.

$$\frac{\partial E^{(i)}}{\partial \sigma^{(0)}} = 0; i = 0,1, \tag{5.4}$$

$$\frac{\partial E^{(i)}}{\partial t^{(o)}} = 0; i = 0,1.... \tag{5.5}$$

Thus, we always differentiate with respect to the unperturbed cluster amplitudes. Solving equations (5.4) and (5.5), we get equations for t and σ respectively. Usually we truncate cluster amplitudes to singles and doubles amplitudes, Thus, we can see here we have twice the number of amplitudes and cluster equations. Equations for left and right amplitudes are coupled.

The first derivative of energy can be written as

$$\begin{aligned} E^{(1)} &= \langle \Phi_0 | e^{\Sigma} (H^{(1)} e^{T})_L | \Phi_0 \rangle_{DL} + \\ &\langle \Phi_0 | e^{\Sigma} (\Sigma^{(1)} H e^{T})_L | \Phi_0 \rangle_{DL} + \langle \Phi_0 | e^{\Sigma} (H e^{T} T^{(1)})_L | \Phi_0 \rangle_{DL} \end{aligned} \tag{5.6}$$

Differentiation of the energy derivative with respect to t and σ gives us equations for the derivative cluster amplitudes.

$$\frac{\partial E^{(1)}}{\partial \sigma^{(0)}} = 0 \tag{5.7}$$

$$\frac{\partial E^{(1)}}{\partial t^{(0)}} = 0 \tag{5.8}$$

General equation to obtain the amplitudes $t^{(1)}$ and $\Sigma^{(1)}$ are given by equation (5.7) and (5.8), At the stationary point derivative energy expression has form

$$E^{(1)}_{stat} = \langle \Phi_0 | e^{\Sigma} (H^{(1)} e^{T})_L | \Phi_0 \rangle_{DL} \tag{5.9}$$

Thus being variational method, the Hellman-Feynman theorem holds good, (2n+1) rule is applicable for evaluating the energy derivatives. Thus to evaluate first order derivative of energy we only require knowledge of $\sigma^{(0)}$ and $t^{(0)}$ respectively.

Stationary condition applied on $E^{(1)}$ with respect to $t^{(0)}$ and $\sigma^{(0)}$ gives the connectivity in the amplitude equation. Similarly, for higher order derivatives using Hellman-Feynman theorem we eliminate the derivative amplitudes of the same order to get the (2n+1) rule. Therefore, the ECC functional not only gives the connected diagrams and terms for energy, but also gives connectedness in energy derivative terms as well. For calculating higher order derivatives of energy i.e. higher order response properties, we require the derivatives of t and σ amplitudes. For instance if we have to calculate the second order derivative of energy then we require only first order derivative of t and σ amplitudes.

5.2.2 Coupled Perturbed Hartree Fock equations (CPHF)

The Coupled Perturbed Hartree Fock equations (CPHF) can be used for solving the equation for each geometry.

$$F^{(0)}C^{(0)} = S^{(0)}C^{(0)}\varepsilon^{(0)} \tag{5.10}$$

$$F^{(1)}C^{(0)} + F^{(0)}C^{(1)} = S^{(1)}C^{(0)}\varepsilon^{(0)} + S^{(0)}C^{(1)}\varepsilon^{(0)} + S^{(0)}C^{(0)}\varepsilon^{(1)} \tag{5.11}$$

$$(F^{(0)} + S^{(0)}\varepsilon^{(0)})C^{(1)} = (F^{(1)} + S^{(1)}\varepsilon^{(0)} + S^{(0)}\varepsilon^{(1)})C^{(0)} \tag{5.12}$$

Equations (5.10) and (5.11) provide give the unperturbed and perturbed SCF equations. $C^{(1)}$ can be obtained from solving these equations and hence $F^{(1)}$ can be calculated.

Fock matrix (F), overlap matrix (S) , coefficient matrix (C) and orbital energy matrix (ε)are expanded in terms of perturbation parameters. Thus we obtain first order CPHF equations by collecting the perturbed terms together. Using orthonormality condition of molecular orbitals $C^{\dagger(0)}S^{(0)}C^{(0)} = 1$,

$$C^{\dagger^{(1)}}S^{(0)}C^{(0)}+C^{\dagger^{(0)}}S^{(1)}C^{(0)}+C^{\dagger^{(0)}}S^{(0)}C^{(1)}=0 \tag{5.13}$$

Thus $F^{(1)}$ term is given as,

$$F^{(1)}=h^{(1)}+G^{(1)}D^{(0)}+G^{(0)}D^{(1)} \tag{5.14}$$

Here in equation (5.14) $h^{(1)}$ represents the one-electron (core) matrix, D is the density matrix, G is the tensor containing two electron integrals. The density matrix can be written as a product of MO coefficients

$$\begin{aligned} D^{(0)} &= C^{\dagger(0)}C^{(0)} \\ D^{(1)} &= C^{\dagger(1)}C^{(0)}+C^{\dagger(0)}C^{(1)} \end{aligned} \tag{5.15}$$

The quantities $S^{(1)}$, $h^{(1)}$ and $g^{(1)}$ are first derivatives of overlap matrix, one and two electron integrals. Simplifying equation (5.12) by substituting $C^{\dagger^{(0)}}S^{(0)}C^{(0)}=1$ and $C^{\dagger^{(0)}}F^{(0)}C^{(0)}=E$ we get the CPHF equation in matrix form.

$$EU^{(1)}-U^{(1)}E=C^{\dagger^{(0)}}S^{(1)}C^{(0)}E-C^{\dagger^{(0)}}F^{(1)}C^{(0)}+E^{(1)} \tag{5.16}$$

The CPHF equations are generally linear and can be solved with standard matrix operations. These equations are solved in iterative manner. The size of U matrix is number of occupied orbitals times number of virtual orbitals. The formulation of CPHF equations can be done either in molecular orbital (MO) basis or atomic orbital (AO) basis.

5.2.3 Gradient calculation using ECC approach

Though ECC is variational with respect to the cluster amplitudes it is not variational with respect to the AO to MO coefficients. To eliminate the coefficient derivatives we need to solve a liner equation similar to Z-vector. The gradient of ECC can be written as,

$$E^{ECCSD(1)} = \sum_{\mu\nu\lambda\sigma} \Gamma_{\mu\nu\lambda\sigma}^{ECCSD} \left\langle \mu\nu \middle| \lambda\sigma \right\rangle^{(1)} + \sum_{\mu\nu} P_{\mu\nu}^{ECCSD} (H_{\mu\nu}^{(1)})$$
$$+\sum_{\mu\nu} W_{\mu\nu}^{ECCSD} S_{\mu\nu}^{(1)} + V_{nuc}^{(1)} \tag{5.17}$$

$H^{(1)}$ and $S^{(1)}$ are the derivative Hamiltonian and overlap matrix in AO basis, $V_{nuc}^{(1)}$ is the derivative nuclear repulsion term. P is the effective ECCD density and W is the energy-weighted density matrices.

$$\Gamma_{\mu\nu\lambda\sigma}^{ECCSD} = \Gamma_{\mu\nu\lambda\sigma}^{S} + \Gamma_{\mu\nu\lambda\sigma}^{NS} \tag{5.18}$$

The total density can be split into separable and non-separable densities.

$$\Gamma_{\mu\nu\lambda\sigma}^{S} = (4 \times P_{\mu\nu}^{SCF} \times P_{\lambda\sigma}^{SCF} + 4 \times P_{\mu\nu}^{SCF} \times P_{\lambda\sigma}^{(ECC)} +$$
$$4 \times P_{\lambda\sigma}^{SCF} P_{\mu\nu}^{ECC} - P_{\nu\lambda}^{SCF} \times P_{\mu\sigma}^{ECC} - P_{\mu\lambda}^{SCF} \times P_{\nu\sigma}^{ECC} -$$
$$P_{\nu\lambda}^{SCF} \times P_{\mu\lambda}^{ECC} - P_{\mu\sigma}^{SCF} \times P_{\nu\lambda}^{SCF} - P_{\mu\lambda}^{SCF} \times P_{\nu\sigma}^{SCF}) \tag{5.19}$$

The non- separable two particle density has various blocks. They are as below

$$\Gamma^{NS} = HHHH + PPPP + HPHP + HHPP + HHHP +$$
$$PHPH + PPHP + PPPH \tag{5.20}$$

. While using $\Gamma_{\mu\nu\lambda\sigma}^{ECCSD}$, is symmetrized as $\mu \leftrightarrow \nu, \lambda \leftrightarrow \sigma, \mu\nu \leftrightarrow \lambda\sigma$ interchange. These are permutational symmetries of electron repulsion integrals (ERIs), with these the $\Gamma_{\mu\nu\lambda\sigma}^{ECCSD}$ is contracted. The MO basis expression one particle density is given as,

$$P_{p,q}^{total} = P_{ij}^{ECCSD} + P_{ab}^{ECCSD} + P_{ia}^{ECCSD} + P_{ai}^{ECCSD} \tag{5.21}$$

All combined densities will together give the total ECCSD density.

$$L_{ai} = \sum_{bj} [(ij\|ab) - (ib\|ja)] P_{bj}^{ECC} + \left(\varepsilon_a - \varepsilon_b\right) P_{ai}^{ECC} \tag{5.22}$$

$$\sum_m \sum_e D_{em} [\langle ei||ma\rangle] + \delta_{im}\delta_{ae}(f_{aa} - f_i) + D_{em}^{*} \langle mi||ea\rangle = -\chi_{ai} \tag{5.23}$$

$$\begin{aligned} &\frac{1}{2}\sum_m \sum_{ef} \langle ef\,||am\rangle \Gamma_{im}^{ef*} - \frac{1}{2}\sum_{mn}\sum_e \langle ie||mn\rangle \Gamma_{mn}^{ae*} + \sum_{mn} D_{mn} \langle im||an\rangle \\ &+ \sum_{ef} D_{ef} \langle ie||af\rangle = \chi_{ai} \end{aligned} \tag{5.24}$$

The relax densities are obtained through equations (5.23) and (5.24). Energy-weighted density matrix is given as,

$$W_{ij}^{(ECCSD)} = \sum_{kab} \Gamma_{jk}^{ab} \left(ki||ab\right) - \varepsilon_i P_{ij}^{(ECCSD)} - \sum_{pq} P_{pq}^{(ECCSD)} \left(ip||jq\right) \tag{5.25}$$

$$W_{ab}^{(ECCSD)} = \sum_{ijc} \Gamma_{ij}^{bc} \left(ij||ca\right) - \varepsilon_a P_{ab}^{(ECCSD)} \tag{5.26}$$

$$W_{ai}^{(ECCSD)} = \sum_{jkb} \Gamma_{jk}^{ba} \left(jk||ib\right) - \varepsilon_i P_{ai}^{(ECCSD)} \tag{5.27}$$

Thus we can write a systematic procedure to calculate gradient. Thus the algorithm can be written as,

1) Do the SCF calculation; calculate AO-ERIs (electron repulsion integrals in AO basis). Store the AO integrals.
2) Transform the AO integrals $\left(ij\|ab\right)$, $\left(ia\|jb\right)$, $\left(ia\|bc\right)$, $\left(ij\|ka\right)$, $\left(ab\|cd\right)$ into MO integrals. Store the MO integrals. Calculate the ECCSD energy.
3) Calculate density matrix, relaxed one particle density and two particle density and weighted density matrices.
4) Perform the back transformation of density from MO to AO basis.

5) Evaluate the gradient using equation (5.16) where the gradient composes of derivatives of kinetic energy, Hellmann-Feynman, Lagrangian, AO integral and total gradient is calculated as sum of these terms.
6) Thus obtaining the gradient calculated through ECCSD density, use this gradient for calculating geometry optimization.
7) We obtain the hessian matrix numerically.
8) The geometry optimization is done using Newton-Rapson Method. The tolerance of gradient is 10^{-6}. The geometry obtained at this gradient value is the optimized geometry.

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Chapter 6

Summary and Future Scope

This chapter gives a summary of the work carried out in the thesis as well as the future scope of the thesis. It gives the brief idea about the importance of (Extended coupled cluster) ECC in predicting the molecular properties using different approximations. The detail discussion about the formulation of gradient by ECC methods is given.

6.1 Summary

The focus of this thesis is to emphasize the role extended coupled cluster method [1-4] in predicting molecular properties of various systems. The accuracy and precision of ECC method at any level of truncation has made it superior than other correlated methods [5-12] for property calculation. The variational nature of the method, which fulfils the (2n+1) rule simplifies the property calculations [13-18]. In particular higher order properties. Thus, with the knowledge of n^{th} order amplitude derivatives, we can calculate $(2n+1)^{th}$ order energy derivatives. The double linked form of the functional ensures the size-extensivity for energy as well as energy derivatives at each truncation. The ECC functional has the inbuilt characteristic property to get naturally terminated. However, natural truncation is at quite high order and hence needs truncation for practical application.

We have used the ECC functional for calculation of IR and Raman intensities along with vibrational frequencies and depolarization ratio[19] . IR and Raman intensities are mixed derivatives of energy with respect to the electric field and geometry. For these calculations, we have used the left exponential truncated up to quadratic terms. The partial triples are implemented in a non-iterative manner. The semi-numerical approach is used for the calculations. The dipole moment and polarizability are calculated using analytic approach while their derivatives with respect to geometry are calculated using numerical approach. The geometric derivatives of polarizability are important for calculating Raman Scattering cross-section. The information of the depolarization ratio gives the idea about the symmetry of vibrations. We have studied the effect of partial triples on IR and Raman intensities for all the test systems except formaldehyde. For Formaldehyde, partial triples are included only for calculation of IR intensities. In particular HF, BH and CH^+ are studied in aug-cc-pVQZ basis to know how the inclusion of partial triples affects the IR and Raman intensities. The vibrational frequencies change marginally due to the inclusion of triples in case of HF and BH molecule. However, for CH^+ IR intensity reduces due to inclusion of partial triples. For HF molecule in aug-cc-pVQZ basis, the IR intensity value calculated is close to basis set limit, calculated using partial triples. Raman intensity for BH increases while for HF and CH^+, Raman intensities are unaffected due to inclusion of partial triples. Depolarization ratio is very sensitive to inclusion of partial triples for HF and CH^+, however, for BH molecule it does not show any change. For strongly correlated systems like CO and H_2CO effect of partial triples is more prominent. For CO molecule we also observed effect of augmentation of the basis set. We observe that there is little change of augmentation on intensity; however the frequencies change with the augmentation. It is observed that the effect of partial triples is more than augmentation for CO molecule. For formaldehyde molecule, for CO symmetric stretch mode, IR intensity is reduced while other two stretching modes of CH_2 are marginally affected with the inclusion of partial triples. We have used harmonic approximation for our calculation of IR and Raman intensities. Thus with the ECC approach, calculated spectroscopic properties match with the experimental values as well as highly accurate theoretical methods wherever available.

The dipole-quadrupole polarizability of methane, tetrafluoromethane, water, ammonia, carbon monoxide and hydrogen fluoride are calculated [20]. Quadrupole moment of acetylene, difluoroacetylene, water and ammonia are also calculated. We have also reported the dipole polarizabilities for all the molecules. The ECCSD approach is used for all the calculations. To compare the difference between previously calculated cubic truncation and inclusion of all double linked terms within ECCSD approximation, we have studied carbon monoxide and hydrogen fluoride molecule at different bond distances. Our results point out the importance of current approximation. We observe, with augmentation of basis set dipole polarizabilities are enhanced while dipole-quadrupole polarizabilities are reduced in general.

The general ECCSD approach has double the number of amplitudes and hence the number of equations compared to the normal coupled cluster methods. This creates problem for the convergence of the equation away from equilibrium. Thus, we implement the decoupled approach within the ECCSD method for calculation of potential energy surface. ECC equations were solved in a coupled as well as decoupled manner. We present results using both the methods[21]. We have compared the results with FCI wherever available. Though both coupled and decoupled ECC approaches contain same number of terms, the decoupled scheme proves a better option away from equilibrium. Since coupled ECC contains 2n number of equations to be solved at stretched geometries it is difficult to converge. However the decoupled scheme takes advantage of considering half the number of equations at a time, thereby reducing the complications in computational calculations. For all the molecules the decoupled scheme behaves well. For N_2 molecule, we have compared our results with CCSD(T) method. Decoupled scheme provides better results for all the systems away from equilibrium. The decoupled ECC method takes care of static correlation to some extent.

The analytic derivatives of energy are important in precise calculation of molecular properties, which is lost in numerical calculations. The first order derivative of energy with respect to molecular geometry is called as gradient while the second order derivative is termed as Hessian. The knowledge of gradient is required for geometry optimization, calculating transition states in chemical reaction pathways and finding maxima, minima on the potential energy surface. We present the formulation of analytic gradient using ECC approach. ECC method being variational in nature, follows (2n+1) rule, that makes the higher order property calculation feasible. We have done the formulation of analytic gradients and used them for geometry optimization.

The future scope of the thesis is, use of analytic gradient in calculating various molecular properties. These properties include spectroscopic properties, calculation of hessian. The gradient of dipole-quadrupole polarizability gives the Vibrational Raman Optical Activity. The hessian is used for calculating vibrational frequencies of the molecule. The maxima and minima on the potential energy surfaces can be identified with the gradient calculation. Thus the analytical derivatives open the gateway for evaluation of wide range of properties.

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