Intermediate Hamiltonian Fock space molecular response properties

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by

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CERTIFICATE

This is to certify that the work presented in this thesis entitled, *"Intermediate Hamiltonian Fock space molecular response properties"* by **Mr. Jitendra Gupta**, for the degree of **Doctor of Philosophy**, was carried out by the candidate under my supervision in the Physical Chemistry Division, CSIR-National Chemical Laboratory, Pune-411008, India. Any material that has been obtained from other sources has been duly acknowledged in the thesis.

Date:

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DECLARATION

I, Mr. Jitendra Gupta, hereby declare that the work incorporated in the thesis entiled "**Intermediate Hamiltonian Fock space molecular response properties**" submitted by me to **University of Pune** for the degree of **Doctor of Philosophy** is original and has not been submitted to this or other University or Institution for the award of Degree or Diploma. Such material, as has been obtained from other sources has been duly acknowledged.

Date:

Place: Pune

Jitendra Gupta

For my Parents, brother and my wife

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Contents

List of Tables

List of publications

1. "Constrained variational approach for energy derivatives in Intermediate Hamiltonian Fock-space coupled-cluster theory" Aryya Ghosh, **Jitendra Gupta**, Sourav Pal, and Nayana Vaval, **Chemical Physics 401**, 45, (2012)

2. "Extended coupled cluster through nth perturbation order for molecular response   properties: A comparative study" **Jitendra Gupta**, P. U. Manohar, Aryya Ghosh, Nayana Vaval and Sourav Pal, Chemical Physics **417**, 45, (2013)

3. "A Lagrange multiplier approach for excited state properties through Intermediate Hamiltonian formulation of Fock space multireference coupled-cluster theory", **Jitendra Gupta**, Nayana Vaval and Sourav Pal, **Journal of Chemical Physics 139**, 074108, (2013)

4. "Partitioned EOMEA-CCSD(2): An Efficient N^5 Scaling Method for Calculation of Electron Affinities" Achintya Kumar Dutta, **Jitendra Gupta**, Himadri Pathak, Nayana Vaval and Sourav Pal, **(Communicated)**

5. "Application of Intermediate Hamiltonian Fock Space Multireference Coupled Cluster Method to Core Excitation Spectra", Achintya Kumar Dutta[a], **Jitendra Gupta**[a], Nayana Vaval and Sourav Pal, **(in preparation)**

Abstract

This thesis is mainly focused on the calculation of molecular response properties using Intermediate Hamiltonian formulation of Fock space multi reference coupled cluster (IHFSMRCC) theory. These properties include excitation energies, excited state properties and the electronic transition dipole moment. Apart from the IHFSMRCC, a variant of variational coupled-cluster i.e. extended coupled-cluster (ECC) method has also been used for the ground state molecular response properties for closed shell systems at equilibrium as well as stretched geometries.

Over the past few decades, coupled cluster methods [1-4] have been established as promising tools for evaluation of correlation energy as well as molecular properties. It introduces the dynamic correlation in efficient way through infinite partial summation of important terms of many body perturbation theories. The linear response approach to the coupled cluster method was originally formulated by Monkhorst [5] and further developed and applied with orbital relaxation built in by Bartlett and coworkers, who introduced the Z-vector [6] technique within the coupled cluster (CC) framework [7] to simplify the energy derivative problem. With the help of Z vector method, energy derivative for each mode of perturbation can be obtained by solving only an additional linear equation, which contains one extra set of perturbation-independent parameters. This algebraic method is however quite laborious and more difficult for higher order derivatives. Jorgensen and coworkers [8] formulated constrained variational approach based on method of Lagrange multipliers. The final equation is shown to be equivalent as the ones obtained through Z vector technique, but this approach is found to be suitable for extension to progressive higher order derivatives.

Parallel to these developments, Pal et al [9-11] also pursued a fully stationary approach to expectation value coupled cluster (XCC). It has been realized that variational methods are quite desirable especially for molecular properties

because of its fulfillment of GHF theorem and (2n+1) rule. Pal and coworkers implemented the variational method which is based on direct variation of suitable energy functional without any constraint [9]. Various forms of energy functional like expectation value (XCC) [9-12], Unitary coupled cluster (UCC) [13, 14] and extended coupled cluster (ECC) [15, 16] have been studied in literature. Among these, ECC has shown to be most promising as well as successful functional in particular for properties.

The idea of ECC functional was first developed by Arponen [15] and then used by Arponen and coworkers [16] in the context of condensed matter physics. Among its many advantageous features, double linked structure of ECC functional is a particular one, which not only ensures a naturally terminating series of energy functional, but also provides a fully connected set of stationary equations for cluster amplitudes even in its approximate versions.

Although ECC functional has naturally terminating series due to its double linking structure, natural truncation occurs at very high powers in excitation and de-excitation amplitudes. Hence ECC functional with singles and doubles requires further approximations to be imposed in order to make it computationally feasible for its larger application. Various forms of approximation schemes has already been implemented and analyzed by several workers [17-19].

A perturbation based analysis generally provides a guideline to identify the importance of individual terms in energy functional. The different variations of UCC and XCC functional known as XCC(n)/UCC(n) have been used for energy calculations by Bartlett and coworkers [12, 13]. These functional contain all the terms correct through a given order n. Similar kind of perturbation based functional for ECC (n) has also been used and analyzed by Kucharaski and Bartlett [20] for correlation energy at the equilibrium as well as stretched geometry.

However, in cases of molecular bond dissociation and open shell states, a multi-reference zeroth order description becomes essential for the treatment of non-dynamic electron correlation and dynamic correlation is taken care of by the built in exponential feature of wave operator. These methods are collectively referred to as multi-reference coupled cluster (MRCC) [21-29] methods. Existing MRCC approaches can be divided into three basic categories: Fock space (FS) [21, 22] or valance universal (VU), Hilbert space (HS) [23] or state universal (SU) and state selective (SS) [24-29] CC. The first two approaches are commonly in the class of multi-root MRCC methods, as they are built on the concept of Bloch equation based effective Hamiltonian [30-31] acting within a model space. It is important to mention here that several methods based on SRCC have been extensively developed, which are widely applicable in quasi-degenerate situations [32-39]. Although these methods structurally differ from MRCC method in many aspects, their high accuracy, relative simplicity and cost effectiveness are important to note.

In this thesis, we focus mainly to the FSMRCC method. [40-53] The FSMRCC method has been successfully used for difference energy calculations. However, in several cases when model space is increased in order to target more excited states, the method faces convergence difficulties. This is termed as intruder state [54, 55] problem. The intermediate Hamiltonian [56] formulation of FSMRCC (IHFSMRCC) [57-60] method provides a more efficient and reliable as well as numerically stable way to handle the intruder state problem.

The idea of intermediate Hamiltonian was first introduced by Malrieu [56] *et al* in the context of degenerate perturbation theory. Various kinds of intermediate Hamiltonian schemes have been developed and implemented by several workers [57-60].

Formulation of efficient theoretical as well computational technique for the evaluation of molecular properties in FSMRCC method is quite desirable in order to increase the scope and applicability of the method. The linear response

in effective Hamiltonian based FSMRCC method was initiated by Pal [61] and then implemented by Pal and coworkers for the first order properties [62, 63]. Ajitha and Pal developed the Z-vector like formalism in FSMRCC [64, 65] framework, which eliminated the highest sector cluster response quantities. The extension of Lagrange multiplier approach (LMA) in FSMRCC theory using complete model space for the first order energy derivatives was initiated by Szalay [66]. This approach was further generalized for general incomplete model space by Shamasundar et al [67, 68] for higher order energy derivatives and also implemented by Pal and coworkers [69-72].

In our opinion, it is desirable to extend the LMA in IHFSMRCC formulation for energy derivatives, in order to obtain excited state properties for desired number of states with bigger basis sets and larger model space in numerically stable and cost effective way. The same is one of the major objectives of this thesis. Apart from the IHFSMRCC method, a variational single reference CC method for efficient evaluation of ground state molecular electric response properties has also been proposed and implemented. The present thesis is organized as follows:

First chapter: In this chapter, we have briefly reviewed the early developments in molecular quantum chemistry especially for electronic structure theory. A general introduction has been provided for both single and multireference methods. The linear response approach has been discussed for single reference and Fock space multi-reference coupled cluster theory. Z-vector and Lagrange multiplier approach for energy derivatives has also been discussed for coupled cluster (CC) methods. Finally, at the end of this chapter, the scope and objectives of this thesis have been discussed.

Second Chapter: In this chapter, we have presented and analyzed the extended coupled cluster (ECC) energy functional, truncated up to nth perturbation order limit to operators of the single and double excitations. The expression for the first order energy derivatives based on the above truncation schemes has been derived and numerically analyzed. We have done a comparative study for

dipole moment in various perturbative ECC (n) methods (2≤n≤5) for three systems (HF, H_2O and BH) at equilibrium geometry. We have particularly studied two variants of ECC (4) and ECC (5*) method for stretched geometry. We have analyzed the contribution of important terms present in ECC functional based on perturbative argument. We have compared our results with standard coupled cluster (CCSD) as well as cubic truncated ECC and also benchmarked with the full CI results wherever available.

Third chapter: in this chapter, we present a formulation based on Lagrange multiplier approach for efficient evaluation of excited state energy derivatives in Fock space coupled cluster theory within the Intermediate Hamiltonian framework. The formulation is applied to derive the explicit generic expressions up to second order energy derivatives for [1, 1] sector of Fock space with singles and doubles approximation. Its advantage, efficiency and interconnection in comparison to the Lagrange multiplier approach in traditional formulation of Fock space, which is built on the concept of Bloch equation based effective Hamiltonian, has been discussed. Computational strategy for their implementation has also been discussed in some detail.

Fourth chapter: In this chapter, we have calculated electronic transition dipole moment (ETDM) through intermediate Hamiltonian formulation of Fock space multi-reference coupled-cluster (IHFSMRCC) theory, which measures absorption intensities. ETDM can be directly obtained through matrix element of one particle electric perturbation operator between ground and excited states. A Lagrange multiplier approach has been used to parameterize the left vector of both the ground and excited states, while the right vector of excited state is obtained through eigenvalue structure of intermediate Hamiltonian matrix. Apart from ETDM, excitation energies have also been calculated through IHFSMRCC in order to relate the ETDM to oscillator strength using dipole length approximation. We have presented the transition dipole moments and oscillator strengths of few molecules and compare our results with values obtained through equation of motion coupled-cluster (EOMCC) method.

Fifth chapter: The Fock space multi-reference coupled cluster (FSMRCC) method provides an efficient approach for direct calculation of excitation energies. In the intermediate Hamiltonian (IH-FSMRCC) formulation, the method is free from intruder state problem and associated convergence difficulties, even for a large active space. In this chapter, we demonstrate that the IH-FSMRCC method with suitably chosen model space can be used for accurate description of core excitation spectra of molecules even with Hartree-Fock orbital for the neutral molecules. We have reported the core excitation energy of three test systems H_2O, N_2 and CH_4. Unlike the EOM based method, the IH-FSMRCC does not require any special technique for convergence. Our preliminary test results shows that the IHFSMRCC method with singles and doubles approximation performs slightly better than the standard EOMEE-CCSD method.

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Chapter 1

Electronic structure theory and linear response: A brief overview

In this chapter, we have briefly reviewed the early developments in molecular quantum chemistry especially for electronic structure theory. A general introduction has been provided for both single and multireference methods. The linear response approach has been discussed for single reference and Fock space multi-reference coupled cluster theory. Z-vector and Lagrange multiplier approach for energy derivatives has also been discussed for coupled cluster (CC) methods. Finally, at the end of this chapter, the scope and objectives of this thesis have been discussed.

1.1 Introduction

Over the past few decades, there have been significant developments in theoretical methods in order to explain several chemical phenomena using the principles of quantum mechanics for atomic and molecular system [1-10]. This has introduced a new branch in literature named as quantum chemistry, which can be further subdivided into two branches: molecular structure [11] and molecular dynamics [12]. Depending on the aim of the study, these sub-branches deal with different aspects of chemistry and the success of molecular dynamics intrinsically depends on the success of molecular structure. Hence, it is extremely desirable to develop efficient theoretical method to determine molecular structure accurately. Development of correlated methods, commonly known as many body methods, were demanded by the failure of mean field approaches like Hartree-Fock (HF) [11, 13-15] method in describing the electronic structure of atomic and molecular systems even qualitatively. Among the several many body methods in literature are configuration interaction (CI) [11,16,17], many-body perturbation theory (MBPT) [18-23] and coupled-cluster (CC) [24-27] methods. These methods are commonly termed as single reference (SR) methods, as these methods involve single dominating configuration to describe closed shell molecular systems. Single reference coupled cluster (SRCC) method [28-37] is now well established as a most promising tool for the accurate treatment of electron correlation effects in cases where a single determinant provides a good zeroth order description. Over the past few decades, SRCC method has been widely applied for the calculation of correlation energy, molecular properties, gradients and potential energy surfaces [33-37]. However, in cases of molecular bond dissociation and open shell states, a multi-reference zeroth order description becomes essential for the treatment of non-dynamic electron correlation and dynamic correlation is taken care of by the built in exponential feature of wave operator. These methods are collectively referred to as multi-reference coupled cluster (MRCC) [39-45] methods. Existing MRCC approaches can be divided into three basic

categories: Fock space (FS) [39, 40] or valance universal (VU), Hilbert space (HS) [41] or state universal (SU) and state selective (SS) [42-47] CC. The first two approaches are commonly in the class of multi-root MRCC methods, as they are built on the concept of Bloch equation based effective Hamiltonian [48, 49] acting within a model space.

This thesis is mainly focused on FSCC method [62-75]. The FSMRCC method has been successfully used for difference energy calculations. However, in several cases when model space is increased in order to target more excited states, the method faces convergence difficulties. This is termed as intruder state [76, 77] problem. The intermediate Hamiltonian [78] formulation of FSMRCC (IHFSMRCC) [79-88] method provides a more efficient and reliable as well as numerically stable way to handle the intruder state problem.

The idea of intermediate Hamiltonian was first introduced by Malrieu [78] *et al* in the context of degenerate perturbation theory. Various kinds of intermediate Hamiltonian schemes have been developed and implemented by several research groups. Meissner has applied the intermediate Hamiltonian technique to reformulate the FSCC method for excitation energy [79-81]. The eigenvalue-independent-partitioning (EIP) [89] technique by Sinha *et al* can also be treated as a specific implementation of intermediate Hamiltonian in Fock space. The IH formulation of FSMRCC, which leads to a completely new method, has been developed and extensively applied by Kaldor and coworkers [90, 91].

Efficient evaluation of molecular properties in FSMRCC method is quite desirable for wider applicability of the method. The linear response in effective Hamiltonian based FSMRCC method was initiated by Pal [92] and then implemented by Pal and coworkers for the first order properties [93, 94]. Ajitha and Pal developed the Z-vector like formalism in FSMRCC [102, 103] framework, which eliminated the highest sector cluster response quantities. The extension of Lagrange multiplier approach in FSMRCC theory using complete model space for the first order energy derivatives was initiated by Szalay [104].

This approach was further generalized for general incomplete model space by Shamasundar et al [105, 106], for higher order energy derivatives and also implemented by Pal and coworkers [107-110].

As mentioned earlier, the traditional effective Hamiltonian based FSMRCC theory suffers from intruder states. The intermediate Hamiltonian formulation of Meissner [79] provides an alternative way to reach the convergence in a more efficient manner with larger model space. This not only helps one to obtain more number of states, but also, in several cases, significantly improves the correlation effects. Apart from the improvements in correlation effects, a considerable amount of computational simplicity arises. Hence, in our opinion, it is desirable to extend the LMA [97, 104, 105] in IHFSMRCC formulation of Meissner for energy derivatives, in order to obtain excited state properties for desired number of states with bigger basis sets and larger model space in numerically stable and cost effective way.

Objective of this thesis is to develop and implement a theoretical formulation for efficient evaluation of molecular response properties for ground and excited states of molecules using coupled cluster methods. In particular, we have formulated and implemented a Lagrange multiplier approach in IHFSMRCC framework for accurate and efficient evaluation of excited state molecular properties. We also present our implementation of a variant of SRCC method for ground state molecular response properties at equilibrium as well as stretched geometry for closed shell molecular systems. We start with presenting a brief overview of some previous developments in many body methods, which will help in demonstrating the relevance of the proposed work. The scope and objective of this thesis will be given at the end of this chapter.

1.2 Atomic and molecular structure theory: A quantum mechanical approach

Atomic and molecular systems are formed due to stable interactions among positively charged nuclei and negatively charged electrons. Electronic structure

of atoms and molecules are described by quantum mechanical bound states and can be studied by solving time-independent Schrodinger wave equation [11, 111].

$$H\Psi = E\Psi \qquad (1.1)$$

Where, H is the Hamiltonian operator for the total energy of the system. The total energy contains the kinetic energy of its constituent particles, the potential energy due to attractive and repulsive interactions amongst the particles and the energy due to interaction of system with surroundings. Interaction of system with surrounding may be quite complicated and can include the effect of external electric field, magnetic field, geometrical distortion, etc. In the absence of external interactions between system and surrounding, kinetic energy of the system can be divided into two parts, namely, nuclear and electronic kinetic energies respectively. The potential energy has three parts: nuclear-electron attraction energy, electron-electron attraction energy and the nuclear-nuclear repulsion energy. For the system of M nuclei and N electrons, Hamiltonian operator can be written as [11],

$$H = -\frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{\|r_i - R_A\|} + \sum_{\substack{i,j \\ i<j}}^{N}\frac{1}{\|r_i - r_j\|} + \sum_{\substack{A,B \\ A<B}}^{N}\frac{Z_A Z_B}{\|R_A - R_B\|} \qquad (1.2)$$

In the above equation, R_A and r_i are the spatial coordinates of A-th nuclei and i-th electron respectively. N-electron wave function is a complicated function of spatial coordinates of nuclei and space-spin coordinates of electrons. The wave function of the system with M-nuclei and N-electrons can be written as $\Psi(R_1,...,R_M,x_1,...,x_N)$. According to Pauli principle, the wave function of a system must be anti-symmetric with respect to the exchange of space-spin coordinates of any two electrons and can be written as,

$$\Psi(x_1,...x_i....x_j,...,x_N) = -\Psi(x_1,...x_j....x_i,...,x_N) \qquad (1.3)$$

The most convenient way to impose the condition of anti symmetry on wave function is to express it as a determinant of N-spin orbital's or linear combination of determinants. One can obtain a complete set of N-electron determinant and therefore the exact wave function of N-electron system, provided the orbital's form complete set.

1.3 Born-Oppenheimer approximation and electronic Hamiltonian

It is extremely difficult to solve the Eigen value Eq. (1.1) using full Hamiltonian as given by Eq. (1.2) even for small systems. Since nuclei are much heavier than electrons, during the electronic motion nuclear framework remains virtually static. Thus one can calculate electronic properties for any constant geometry. This is commonly known as frozen-nuclei Born-Oppenheimer approximation (BOA). Under the Born-Oppenheimer approximation, kinetic energy of nuclei vanishes and the nuclear-nuclear repulsion energy becomes constant. Addition of any constant to an operator does not does not change the Eigen functions but simply adds to the Eigen values. Hence, as a consequence of BOA, problem of total Hamiltonian Eigen-value problem can be reduced as a problem of electronic Hamiltonian, which can be written as,

$$H_{el} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{\|r_i - R_A\|} + \sum_{\substack{i,j \\ i<j}}^{N}\frac{1}{\|r_i - r_j\|} \tag{1.4}$$

1.4 Basic criteria for model molecular structure theory

It is important to note that even after using BOA, it is difficult to solve the eigen value problem for electronic Hamiltonian due to presence of inter electronic repulsion term. Hence, we need to use further approximation. Though accuracy of the approximate method can be improved systematically, the method should satisfy some basic conditions at all the stages so that it might be considered as a theoretical model for electronic calculations. These criteria, as were proposed by Pople et. al. [112] about forty five years ago and

quoted after studies and modifications by Bartlett [24] in one of his reviews, can be briefly discussed as follows.

1. The method should be independent of certain choices of configurations and symmetry and should be applicable on wide range of molecular systems

2. The method should be invariant with respect to classes of transformations. Particularly, unitary transformations should not change the orbital degeneracy.

3. The method should be size-consistent. If the energy obtained through a method for a composite system is equal to the summation of energies obtained through the same method for its constituent subsystems at non interacting limit, the method is said to be size-consistant.

4. The method should be size-extensive, which means that the energy of a strongly interacting many electron system for a given nuclear framework should be approximately proportional to the number of electrons.

5. The method should be computationally efficient as well cost-effective, in order to extend its applicability to molecular systems of chemist's interest.

6. The method should be applicable for open shell systems and excited states.

Among these, size-consistency and size-extensivity are the most important criteria as, the efficiency and accuracy of the method are determined by these factors.

1.5 Hartree-Fock theory

Hartree-Fock method [11, 13, 14] is the most fundamental method among all of the methods to obtain approximate solution of electronic Hamiltonian based Schrodinger equation. Hartree-Fock theory is based on the approximation that

the ground state of closed shell atoms and molecules can be described by a single determinant configuration.

$$\Phi_0(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_1(x_2) & \cdots\cdots & \chi_1(x_N) \\ \chi_2(x_1) & \chi_2(x_2) & \cdots\cdots & \chi_2(x_N) \\ .. & & .. & .. \\ \chi_N(x_1) & \chi_N(x_2) & \cdots\cdots & \chi_N(x_N) \end{vmatrix} \tag{1.5}$$

Electrons are assumed to be independent of each other and each electrons move in a spherically averaged inter-electronic repulsion potential due to other (N-1) electrons. Thus, HF theory is also known as independent particle model. According to variation principle, the best wave function of the form given by Eq. (1.5) is the one, which provides the minimum energy.

$$E_0 = \langle \Phi_0 | H_{el} | \Phi_0 \rangle \tag{1.6}$$

Variational optimization of wave function is performed with the choice of orthonormal spin orbitals, which leads to integro-differential equations known as Hartree-Fock equation. Hartree-Fock equation has to be solved in iterative manner.

$$f(x)\chi_a(x) = \varepsilon_a \chi_a(x) \tag{1.7}$$

$$f(x) = T_e + V_{ne} + V_{HF}(x) \tag{1.8}$$

$$= -\frac{1}{2}\nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{\|r - R_A\|} + V_{HF}$$

$$V_{HF}(x) = \sum_{j=1}^{N} J_j(x) + \sum_{j=1}^{N} K_j(x) \tag{1.9}$$

$$J_j(x)\chi_i(x) = \int dx' \frac{\chi_j^*(x')\chi_j(x')}{|x - x'|}\chi_i(x) \tag{1.10}$$

$$K_j(x)\chi_i(x) = \int dx' \frac{\chi_j^*(x')\chi_i(x')}{|x-x'|}\chi_j(x)$$

<div align="right">(1.11)</div>

Here, the $f(x)$ is Fock operator [11] which is an effective one electron operator. The operator $v_{HF}(x)$ is average potential experienced by an electron due to all other electrons. It includes the average Coulomb interaction $J_j(x)$ and exchange interaction $K_j(x)$. The exchange potential is the consequence of the anti-symmetric nature of wave function.

For atoms, the HF equations can be exactly solved as integro-differential equation. However, for molecules the explicit integration of the two electron interaction term is difficult as the orbitals involved are centered at different nuclei. To overcome this problem, Roothan [15] introduced the idea of basis set expansion. For closed shell systems, the spin orbitals with opposite spin functions are paired up and the problem can be simplified by using only spatial orbitals after spin integration. This method is known as restricted HF (RHF). The open shell systems also have most of the electrons paired up and can be solved by Restricted Open-shell HF (ROHF) method. HF equations can also be explicitly solved using spin orbital's which is called Unrestricted HF (UHF). RHF determinant is a pure eigen function of total spin square operator, while linear combination of suitably chosen ROHF determinants can be adapted to be the eigen function of spin square operator. However, UHF determinant is neither a eigen function nor it can be spin adapted in general.

Though HF theory treats electron-electron repulsion as an average way, it recovers almost 99% of the total energy. The difference between exact energy and HF energy is called correlation energy. The correlation energy can be recovered by improving the approximations used in HF theory leading to various level of theory collectively termed as many-body methods. However HF determinant provides a good starting point for the many-body theories.

1.6 Configuration Interaction method

HF theory provides the best possible single determinant form of wave function and predicts the energy of the systems with reasonable accuracy. However, most of the chemical phenomena like binding energy, excitation energy, activation energy, etc. require the energy difference rather than absolute energy of a specific state. Unfortunately, the variation principle does not hold for energy differences. In order to explain chemical phenomena, we need further to go beyond HF approximation and treat the electron correlation effects correctly. Configuration Interaction (CI) [11, 16, 17] is one of the methods to achieve this.

CI is the simplest and the most traditional method, where the wave function is expressed as a linear combination of Slater determinants and the coefficients are determined by a linear variation method. CI wave function is given by,

$$\Psi = \Phi_0 + \sum_{i,a} C_i^a \Phi_i^a + \sum_{\substack{i<j \\ a<b}} C_{ij}^{ab} \Phi_{ij}^{ab} + \ldots\ldots\ldots\ldots \tag{1.12}$$

Where, Φ_0 is the Hartree-Fock determinant and Φ_i^a and Φ_{ij}^{ab} are the singly and doubly excited determinants respectively. Here, (i, j, ..) and (a, b, …) denote the occupied and unoccupied orbitals respectively in reference (HF) determinant. Also the intermediate normalization convention $\langle \Phi_0 | \Psi \rangle = 1$ has been used.

When all possible determinants in a given one particle basis are included in the wave function, the method is called as full CI (FCI). This produces exact results in a given basis set. Since, FCI is not feasible even for the small and medium size molecules in some meaningful basis, we require approximation like truncated expansions in a CI wave function. CI is a variational method hence, it provides a variational upper bound. Truncating the CI space only up to singly and doubly excited determinants along with the reference HF determinant leads to CISD approximation. Use of linear variation method to

determine the expansion coefficient leads to eigenvalue problem for the Hamiltonian matrix defined over all the determinants present in approximate CI wave function. Matrix elements of Hamiltonian between any two determinants can be evaluated using Slater-Condon rules [11]. Lowest eigenvalue and eigenvector of CI Hamiltonian matrix correspond to the ground state and rest of the eigenvalues and eigenvectors correspond to different excited states. It is well known that any approximate or truncated form of CI is not generally size-extensive and does not separate into appropriate fragments.

There has been developed more advanced approaches in recent years for the solution of CI equation. Notable amongst them are use of configuration state function (CSF) [16, 17], Davidson iterative diagonalisation [113], direct CI [114] etc. The CSF is based on using the spin adapted N-electron function. Two approaches are commonly used to obtain the CSF, namely unitary group approach (UGA) [115, 116] and symmetric group approach (SGA) [116, 117].

A method closely related to CI is the multi-configuration self-consistent field (MCSCF) [118, 119] method. An MCSCF wave function has the truncated CI like expansion where only a small number of selected determinants important for the description of a state are included. In MCSCF method, both the expansion coefficients and the orbitals are optimized to obtain energy which leads to equations similar in structure to the HF equation and are solved by a SCF approach. A variant of MCSCF known as complete active space SCF (CAS-SCF) [120] method is commonly used as a starting point for several multi-reference correlated methods. Selection of determinants to be included in the expansion is carried out by identifying a set of orbitals known as active or valance orbitals. Distributing a given number of valence electrons among all the valance orbitals, we obtain all the determinants that need to be included in the MCSCF expansion. There are several other variants of MCSCF method based on generalization of valance bond approach of Heitler and London.

1.7 Many body perturbation theory

Many body perturbation theory (MBPT) [18-23] is a different systematic procedure for incorporating dynamic correlation effects and producing energy in a size- extensive manner at each order of the theory. In this approach, the exact Hamiltonian is partitioned into two parts, a zeroth order part (H_o) whose solutions are usually known and a perturbation part (V). The perturbation part (V) is assumed to be very small compared to the zeroth order part. There are two different perturbation series one based on Rayleigh Schrödinger (RSPT) [18, 20, 21] and another based on Brillouin Wigner perturbation theory (BWPT) [20]. In both the perturbation series, the wave function is expressed as a power series around the solutions of the zeroth order Hamiltonian. Correction to the wave function at each order is written in terms of the eigenfunctions of H_o. In Brillouin Wigner theory the energy expression depends on the energy itself and hence, an iterative procedure has to be adopted to get the energy. Each successive iteration produce energy at higher order, which is not size-extensive. Hence, BWPT is not usually followed to obtain the correlation energy. Depending on the partitioning of the Hamiltonian, there are two different variants of RSPT: Moller-Plessette (MP) and Epstien-Nesbet perturbation theory. It can be shown that MP partitioning in a RSPT framework leads to a perturbation series which scales correctly with number of electrons (N). This size extensive series is known as MBPT series. This scaling property was first observed by Brueckner [121] for infinite nuclear matter. For the first few orders, Bruckner could show that the terms, which are proportional to the square or higher power of N, cancel among each other at every order. However, he could not prove it for higher orders. Goldstone [122] devised a diagrammatic approach to show that the terms which have incorrect scaling can be represented by unlinked diagrams. He proved that such unlinked diagrams cancel among themselves at each order of perturbation. This is the famous linked diagrams theorem. The application of the diagrammatic approach to atoms was done by Kelly [123]. Finite order MBPT has been extensively used

for correlation energies of atoms and molecules. In MBPT, we construct the zeroth order Hamiltonian as the sum of Fock operators and the perturbation (V) is the full electron-electron repulsion $1/r_{ij}$ term without the spherical average part, which is included in the definition of H_0. Even though the MBPT gives size-extensive results at each order, the slow convergence of the perturbation series is well known. To avoid the convergence problem, non perturbative methods are more desirable.

Now days, the accuracy of any many-body method can be measured in terms of the perturbation order. Thus, MBPT offers a very efficient tool for calibrated measurement of accuracy of energy as well as wave function. The MP based RSPT is now commonly used for correlated calculations of atoms and molecules. The acronyms MP2, MP4, MBPT (n), etc. have become very popular because of accuracy and relative simplicity of the method.

1.8 Independent pair approximation

It is well known that the pair theories play central role in correlation methods. Because of Pauli's exclusion principle and the two particle nature of the Hamiltonian, electron pair theories serve a good approximation for N electron atomic and molecular problem. The simplest of these pair theories considers only one electron pair at a time. Thus a N electron problem is reduced to $N*(N-1)/2$ electron pairs. The interactions among the pairs are neglected. The total correlation energy can be represented as the sum of the pair contributions, which are obtained independently by solving effective two electron equations. This decoupling of pairs is known as the independent electron pair approximation. It was developed by Sinanoglu [124] and Nesbet [125] independently. Sinanoglu obtained this by partial variation and called his theory coupled pair many electron theory, while Nesbit called his theory as Bathe Goldstone theory. Relation between IEPA and perturbation method has been extensively reviewed by Freed [126] and Robb [127]. The IEPA wave function for the pair ij may be written as,

$$\left|\Psi_{ij}\right\rangle = \left|\Phi_0\right\rangle + \sum_{a<b} C_{ij}^{ab}\left|\Phi_{ij}^{ab}\right\rangle \tag{1.13}$$

Where, i, j are the occupied orbital and a, b are the unoccupied (virtual) orbital in the Hartree-Fock determinant. Linear variation method can be used to calculate the energy E_{ij} which is a sum of Hartree-Fock energy and the pair correlation energy corresponding to the pair ij.

$$E_{ij} = E_0 + e_{ij}^{IEPA} \tag{1.14}$$

The total correlation energy in IEPA approximation is defined as,

$$E_{corr}^{IEPA} = \sum_{i<j} e_{ij}^{IEPA} \tag{1.15}$$

Although, the correlation energy for each pair is obtained through linear variation, the sum is not the upper bound to the exact correlation energy. Computationally, IEPA is equivalent to DCI for each pair separately and hence, it is also called "pair-at-a-time" CI. While, DCI is not size extensive, IEPA gives size extensive result. The major disadvantage of IEPA is that it is not invariant to unitary transformation.

1.9 Coupled electron pair approximation

IEPA is based on two approximations. The first one is the neglect of the pair coupling terms and the second one is the assumption that the non-linear terms cancel with part of the energy terms. W. Meyer [128] proposed a series of schemes, which considered the coupling between the pairs. These are known as various versions of coupled electron pair approximation (CEPA) [129-131]. Some of them provide size-extensive results. CEPA takes care of the pair interaction terms neglected in IEPA, but neglects most of the non-linear terms.

1.10 Coupled cluster theory

The coupled cluster (CC) method is now well established as a method of first choice in electronic structure theory. It was first introduced in nuclear physics by Coester and Kümmel [29]. The coupled cluster theory in electronic structure theory was developed from the pair correlation theory of Sinanoğlu [124] and Nesbet [125]. Hubbard [132] applied diagrammatic MBPT and showed that the exact ground state wave function of many-electron system can be written in an exponential form. The coupled cluster theory was first introduced by Cizek and Paldus [28] in electronic structure theory in its present standard form.

The dynamical electron correlation in CC wave function is brought in through an exponential wave-operator operating on the reference function. Usually but not necessarily the HF determinant is considered as reference wave function. In coupled cluster theory, the wave function is expressed as:

$$\left|\Psi_{cc}\right\rangle = e^{T}\left|\Phi_{0}\right\rangle \tag{1.16}$$

Usually, intermediate normalization scheme is used for wave function. Here T is known as cluster operator. The cluster operators commute to each other. In terms of diagrammatic representation, the cluster operators T contain only the upward open connected diagrams. The cluster operators can be written as sum of electron-excitation operators, *viz*, one-electron, two-electron, etc.

$$T = T_1 + T_2 + T_3 + \ldots + T_N \tag{1.17}$$

With,

$$T_1 = \sum_{i,a} t_i^a a_a^+ a_i$$

$$T_2 = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i$$

.

$$T_N = \sum_{\substack{i>j>k.... \\ a>b>c....}} t_{ijk..}^{abc..} a_a^+ a_b^+ a_c^\dagger a_k a_j a_i \tag{1.18}$$

The N-body cluster operator, T_N acting on vacuum $|\Phi_0\rangle$ produces N-tuply hole-particle excited determinant.

Since in Equation (1.16) only one single determinant is taken as a reference function, this method is known as single reference coupled cluster method (SRCC). Since in the limit of all excitations CC theory must be equal to full CI,,we can express the relationship between CI and CC coefficients as,

$$C_1 = T_1$$

$$C_2 = T_2 + \frac{1}{2!} T_1^2$$

$$C_3 = T_3 + T_1 T_2 + \frac{1}{3!} T_1^3 \tag{1.19}$$

$$C_4 = T_4 + T_1 T_3 + \frac{1}{2!} T_2^2 + \frac{1}{4!} T_1^4$$

Substituting Equation (1.16) into Schrödinger equation with normal ordered Hamiltonian leads to:

$$H_N e^T |\Phi_0\rangle = \varepsilon_{corr} e^T |\Phi_0\rangle \tag{1.20}$$

Projecting from left of Equation (1.20) by $|\Phi_0\rangle$ and other excited determinants ($|\Phi_{ij...}^{ab...}\rangle$) separately, we get equations for the correlation energy and amplitudes.

$$\langle \Phi_0 | H_N e^T |\Phi_0\rangle = \varepsilon_{corr} \langle \Phi_0 | e^T |\Phi_0\rangle \tag{1.21}$$

Expanding the right hand side of Eq. (1.21), only the term survive, which does not contain T due to normalization condition. Hence, the Eq. (1.21) can be written as,

$$\left\langle \Phi_0 \left| H_N e^T \right| \Phi_0 \right\rangle = \varepsilon_{corr} \tag{1.22}$$

$$\left\langle \Phi_{ij\ldots}^{ab\ldots} \left| H_N e^T \right| \Phi_0 \right\rangle = \varepsilon_{corr} \left\langle \Phi_{ij\ldots}^{ab\ldots} \left| e^T \right| \Phi_0 \right\rangle \tag{1.23}$$

The correlation energy and the cluster amplitudes can be obtained through Eqs. (1.22) and (1.23).

Both the left and right side of Eq. (1.23) have connected as well as disconnected terms Due to presence of e^T term, the unlinked terms of both sides of Eq. (1.23) get mutually canceled. The disconnected terms of Equation (1.23) for double excitations can occur as product of connected single excitation terms $\left\langle \Phi_i^a \left| H_N e^T \right| \Phi_0 \right\rangle_{open,connected}$ with singly excited cluster amplitude $\left(t_j^b \right)$ disappears from final equations. In the same way, the connected, open terms survive in Equation (1.23), leading to completely connected CC equations. Thus, Eqs. (1.22) and (1.23) can be written as,

$$\varepsilon_{corr} = \left\langle \Phi_0 \left| H_N e^T \right| \Phi_0 \right\rangle_{closed,connected} \tag{1.24}$$

$$\left\langle \Phi_{ij\ldots}^{ab\ldots} \left| H_N e^T \right| \Phi_0 \right\rangle_{open,linked} = 0 \tag{1.25}$$

Because of commutation relation, there is no contraction among the cluster operators. This means that in CC diagrams, each cluster operator in the diagram should be connected with Hamiltonian vertex and not with each other. Due to two particle nature of the Hamiltonian operator, it can have maximum four number of contractions with cluster operators. Therefore, the CC equations are algebraic non-linear equations in unknown cluster amplitudes and are at most of quatric power. On the other hand, from Eq. (124), the correlation energy contains only one-body and two-body cluster operators, which are coupled to higher-body cluster operators through Eq. (1.25).

The above CC equations can be derived in another way by pre-multiplying Eq. (1.20) by e^{-T} as,

$$e^{-T}H_N e^T |\Phi_0\rangle = \varepsilon_{corr} |\Phi_0\rangle \tag{1.26}$$

Thus, Eq. (1.26) can be viewed as an eigen value equation for the similarity transformed Hamiltonian, $\bar{H} = e^{-T}H_N e^T$. As, the similarity transformation does not change its eigen values, Eqs. (1.24) and (1.25) can be derived by following the same procedure and we get the following set of equations,

$$\varepsilon_{corr} = \langle \Phi_0 | e^{-T}H_N e^{T} |\Phi_0\rangle \tag{1.27}$$

$$\langle \Phi_{ij....}^{ab....} | e^{-T}H_N e^{T} |\Phi_0\rangle = 0 \tag{1.28}$$

Using Campbell-Baker-Hausdroff (CBH) formula, $e^{-T}H_N e^T$ can be expanded as,

$$\bar{H} = e^{-T}H_N e^T = H_N + \left[H_N, T \right] + \frac{1}{2!}\left[\left[H_N, T \right], T \right] +$$

$$\frac{1}{3!}\left[\left[\left[H_N, T \right], T \right], T \right] + \frac{1}{4!}\left[\left[\left[\left[H_N, T \right], T \right], T \right], T \right] + ... \tag{1.29}$$

Due to the two body nature of H_N and commutative nature of cluster operator, this series can be shown to be terminated after four fold commutations. The connected nature of correlation energy and cluster amplitudes are explicitly revealed by the presence of commutators Eq. (1.29), with H_N being connected, its commutation with cluster operators, generates only connected terms. This eventually leads to a completely connected series.

The Eq. (1.25) leads to a coupled set of nonlinear simultaneous equations, which are solved iteratively to obtain the cluster amplitudes. Perturbation analysis of the iterative procedure shows that at every iteration, the functional gains corrections from various orders of perturbations. After the self-consistency and numerical accuracy is attained, the correlation energy is obtained using Eq. (1.24). If the T contains all possible excitation operators i.e. up to T_N for N-electron system then the method is called full CC (FCC), which

is equivalent to FCI. Obviously, the numbers of cluster operators are same as CI operators. However, the simplicity of CI is lost in case of FCC due to exponential nature of the wave operator and hence, is never used in practice. The most commonly used CC anasatz is to define $T = T_1 + T_2$ leading to singles and doubles (SD) approximation [133, 134]. Unlike CISD, CCSD (or in general, any truncated CC) continues to be size-consistent. This is because of the exponential nature of the wave operator, which includes higher excitations through the products of T_1 and T_2. The CCSD anasatz can be further improved by perturbative or complete inclusion of triples, (CCSD(T) and CCSDT) [135, 136], quadrupoles (CCSDT(Q) and CCSDTQ) [137], etc. These anasatz are seen to further accelerate the convergence the results towards the exactness.

1.11 Alternate Single Reference CC approaches

The standard coupled cluster method just discussed is also known as normal coupled cluster method. Normal coupled cluster (NCC) or single reference coupled cluster (SRCC) method is neither variational, nor perturbative. Due to its non variational nature it seems to be computationally unattractive for energy derivatives. An alternate way is to cast the coupled cluster equation in a variational framework. The direct advantage of casting the CC equations variationally is that, it fulfills the Hellmann-Feynman theorem and (2n+1) rule. This makes the method attractive for higher order energy derivatives. Expectation value CC (XCC), unitary CC (UCC) and extended CC (ECC) are among the methods used in stationary or variational CC theory. We will review these methods in following subsections.

1.11.1 Expectation value CC (XCC) and unitary CC (UCC)

In variational CC approach energy functional are being optimized with respect to cluster amplitudes. In expectation value CC (XCC) [138-140] method, energy functional can be expressed as expectation value of Hamiltonian.

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

(1.30)

$$= \frac{\langle \Phi_0 | e^{T^\dagger} H e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle}$$

Here $T^\dagger$ is hole-particle destruction operator. The functional is Hermitian but it forms a non-terminating series. It is shown by Pal *et al.* [138] that the functional can be written as:

$$E = \langle \Phi_0 | e^{T^\dagger} H e^T | \Phi_0 \rangle_{conn}$$

(1.31)

The above energy expression is a non-terminating series and needs to be truncated for any practical application. Pal et. al. [139] proposed a truncation of the series after some total power of excitation and de-excitation cluster operators. Though energy functional has connected terms, the equation for cluster amplitudes contains disconnected diagrams. Bartlett and co-workers [140] used truncation scheme in XCC based on nth perturbation order i.e. XCC(n). The perturbative truncation scheme ensures size extensivity at each order, as the disconnected terms in the equation of cluster amplitudes mutually cancel.

Van Vleck [141], Primas [142] and Kutzelnigg [143] proposed another approach in variational CC method called unitary coupled cluster (UCC) method. In UCC, the functional is given by:

$$|\Psi_{ucc}\rangle = e^\sigma |\Phi_0\rangle$$

(1.32)

Here, σ is anti-hermitian. σ is chosen as $\sigma = T - T^\dagger$. $\sigma^\dagger = T^\dagger - T$ and $\sigma^\dagger = -\sigma$. Cluster amplitudes may be obtained by using variational or non-variational amplitudes. The non-variational approach is closely related to NCC approach and the set of equations can be obtained by replacing the T in the NCC equations by σ.

Kutzelnigg [143] proposed that UCC can be solved variationally. The energy function in UCC functional can be written as:

$$E = \frac{\langle \Phi_0 | e^{-\sigma} H e^{\sigma} | \Phi_0 \rangle}{\langle \Phi_0 | e^{-\sigma} e^{\sigma} | \Phi_0 \rangle}$$
$$= \langle \Phi_0 | e^{-\sigma} H e^{\sigma} | \Phi_0 \rangle$$

(1.33)

Thus, the UCC equation becomes similarity transformed like NCC, but the σ amplitudes are obtained variationally like XCC. Bartlett and Noga used UCC (n) [140] ansatz analogous to XCC (n). However, unlike XCC (n), UCC (n) functional is symmetric.

1.11.2 Extended coupled-cluster (ECC) method

The similarity transformed form of the NCC ansatz provides a compact tool for developing algorithms for ground state energy. Arponen [144] extended this feature by adding one more similarity transformation on Hamiltonian using hole particle de-excitation operators,

$$E_0^{corr} = \langle \Phi_0 | e^{S} e^{-\tau} H_N e^{\tau} e^{-S} | \Phi_0 \rangle$$

(1.34)

The above equation is known as extended coupled cluster (ECC) [145-150]. In Equation (1.34) τ is known as hole-particle creation operators like T operators in NCC. On the other hand S operator is just the hole-particle destruction operator analogous to $T^{\dagger}$ operators used in XCC, but not conjugate with τ. After double similarity transformation the final form of ECC functional is:

$$E_0^{corr} = \langle \Phi_0 | e^{S} [H_N e^{\tau}]_{linked} | \Phi_0 \rangle_{Double\ linked}$$

(1.35)

The first linking is contraction between τ and H. Double linking [142] implies that the S operator, if not directly connected to the Hamiltonian, must contract with least two distinct τ operators. The double linking ensures the connectedness of the terms of the equations for S and τ, which are obtained by making the energy stationary with respect to t and s amplitudes separately.

ECC insures size extensivity. Piecuch and Bartlett [151] tested the size extensivity of ECC long back.

1.11.3 Equation-of-motion coupled cluster (EOM-CC) method

The equation of motion (EOM) method [152] provides a straightforward and general way to obtain direct energy differences in quantum chemistry. In EOM method, we consider the Schrodinger equation of a system for two different eigenstates simultaneously: one is commonly the ground state Ψ_0 and another is the target or excited state Ψ_k.

$$H\Psi_0 = E_0\Psi_0 \quad \text{and} \quad H\Psi_k = E_k\Psi_k \tag{1.36}$$

With the help of EOM method, we can obtain the energy difference between ground and excited state

$$\omega_k = E_k - E_0 \tag{1.37}$$

Using the normal product form of the Hamiltonian, the above eqns. Become

$$H_N\Psi_0 = \Delta E_0\Psi_0 \; and \; H_N\Psi_k = \Delta E_k\Psi_k \tag{1.38}$$

Where, $\Delta E_0 = E_0 - \langle \Phi_0|H|\Phi_0 \rangle$ and $\Delta E_k = E_k - \langle \Phi_0|H|\Phi_0 \rangle$. But, the energy difference is still given by the same eqn. (1.37), as the same reference energy is being subtracted from both E_0 and E_k.

In EOM-CC [55-57] approach, ground and excited states are parameterized by,

$$\left|\Psi_0\right\rangle = e^T\left|\Phi_0\right\rangle \text{ and } \left|\Psi_k\right\rangle = R_k\left|\Psi_0\right\rangle \tag{1.39}$$

$$R_k = r_0(k) + \sum_{ia} r_i^a(k)\left\{a^\dagger i\right\} + \sum_{\substack{a<b \\ i<j}} r_{ij}^{ab}(k)\left\{a^\dagger i b^\dagger j\right\} + \text{.........} \tag{1.40}$$

As, R_k and T both are the excitation operators, they commute to each other. Using this fact and eqn. (1.38) we obtain,

$$H_N e^T R_k |\Phi_0\rangle = \Delta E_k e^T R_k |\Phi_0\rangle \qquad (1.41)$$

Multiplying Eq. (1.41) on the left with e^{-T}, we find

$$\overline{H}_N R_k |\Phi_0\rangle = \Delta E_k R_k |\Phi_0\rangle \qquad (1.42)$$

The above eqn. has the CI like eigenvalue structure, where the bare normal product Hamiltonian has been replaced with a similarity transformed normal product Hamiltonian. Consequently, within the EOM-CCSD [55-57] approximation, excitation energy can be directly obtained by diagonalising the $\overline{H}_N$ operator within the space spanned by the singly and doubly excited determinants. It is important to note that by simply modifying the structure of R_k, one can also target the ground as well as excited states of $N\pm1$ electron system and the method is denoted as IP/EA-EOMCC [153, 154] method.

1.12 Linear response method for atomic and molecular properties

Hamiltonian of a system interacting with a small time-independent uniform external perturbation g is a complicated function of g which can be expressed as a Taylor series of g. However, for small perturbations, the higher order derivatives of Hamiltonian are negligible. Hence, the Hamiltonian can be considered as linear function of g. The resulting method of obtaining derivative eigenfunctions and eigenvalues is therefore referred to as LR.

$$H(g) = H(0) + g\hat{O} \qquad (1.43)$$

In the above equation, $H(0)$ reads total electronic Hamiltonian in absence of external perturbation. The operator $\hat{O}$ is proportionality constant and resembles to the first order property. For uniform external electric field, $\hat{O}$ will correspond to electric dipole moment operator. As a result, the quantities $\Upsilon = \{E, \Psi\}$ also become perturbation dependent and can be expressed as a Taylor series expansion of g.

$$\Upsilon(g) = \sum_k \frac{1}{k!} g^k \Upsilon^{(k)} \tag{1.44}$$

In above equation, $\Upsilon^{(k)}$ read k-th order derivative of Υ evaluated at zero field. For example, in case of electric field, it corresponds to permanent electric dipole moment, dipole polarizability and first hyperpolarizability for $k = 1, 2, 3$, respectively. Using the above relations, molecular properties may be obtained in two ways. A straight forward method is to solve Schrodinger equation for the system of interest at various field values and obtain the numerical derivatives of energy by finite difference method. This approach is known as finite field approach and requires very accurate evaluation of energy, although, no computational developments are required. Alternately, the molecular properties may be obtained analytically. In analytical method, explicit expressions for energy and wave function derivatives are solved and used to obtain molecular properties. This is a well established fact that an exact wave function follows Hellmann-Feynman theorem.

$$\frac{\partial}{\partial g} \int \Psi(g) \hat{A}(g) \Psi(g) d\tau = \int \Psi(g) \frac{\partial \hat{A}}{\partial g} \Psi(g) d\tau \tag{1.45}$$

The theorem can be generalized for higher order derivatives. The generalized Hellmann-Feynman theorem says that with the knowledge of wave function and its derivatives up to n-th order, one can obtain analytically, the response properties up to $(2n+1)$-th order. This is the famous $(2n+1)$-rule used in the context of analytical response properties. For a general non-exact wave function, the Hellmann-Feynman theorem and its generalized form are not applicable. However, if the wave function is obtained variationally, it can be easily shown that the wave function obeys the generalized Hellmann-Feynmann theorem. Hence, in electronic structure theories, emphasis is given on stationarity of the wave functions.

1.13 Linear response approach in SRCC theory

The linear response (LR) approach in SRCC method was initiated by Monkhorst [33(a)]. In presence of a uniform external field, the SRCC wave function can be expanded in Taylor series of g as given in Eq. (1.44). The expressions for derivatives of energy and wave functions are obtained by differentiating Eq. (1.24) and Eq. (1.25) with respect to the external field g up to desired order. The equations for the given order are linear in derivative cluster amplitudes of that order. The expressions for first order correlation energy and cluster amplitude derivative, neglecting the orbital relaxation are given below

$$E_0^{corr(1)} = \left\langle \Phi_0 \left| [(\hat{O}e^T)_c + (H_N e^T T^{(1)})_c] \right| \Phi_0 \right\rangle \tag{1.46}$$

$$0 = \left\langle \Phi^* \left| [(\hat{O}e^T)_c + (H_N e^T T^{(1)})c \right| \Phi_0 \right\rangle \tag{1.47}$$

The SRCC-LR method described above is conceptually very simple and straightforward. However, for each mode of perturbation, one has to obtain the wave function derivative which makes the method practically cumbersome, particularly for higher order properties. NCC-LR can be solved more efficiently by circumventing the solution of wave function derivatives to the extent possible.

Based on Dalgarno's interchange theorem [155], Bartlett and co-workers [156, 157] introduced the Z-vector technique in NCC-LR. The idea was taken from Handy and Schaefer [95] who used the technique for analytical derivatives for CI method. We rewrite Eq. (1.46) and Eq. (1.47) in a compact form as

$$\varepsilon^{corr(1)} = Y^T T^{(1)} + Q(O) \tag{1.48}$$

$$0 = AT^{(1)} + B(O) \tag{1.49}$$

Where,

$$Y^T T^{(1)} = \left\langle \Phi_0 \middle| \left(H_N e^T T^{(1)} \right)_c \middle| \Phi_0 \right\rangle$$

$$Q(O) = \left\langle \Phi_0 \middle| \left(O e^T \right)_c \middle| \Phi_0 \right\rangle$$

$$A T^{(1)} = \left\langle \Phi^* \middle| \left(H_N e^T T^{(1)} \right)_c \middle| \Phi_0 \right\rangle$$

$$B(O) = \left\langle \Phi^* \middle| \left(O e^T \right)_c \middle| \Phi_0 \right\rangle$$

Introducing Z^T, independent of perturbation, and defining this as follows:

$$Z^T A = Y^T \qquad (1.50)$$

Substituting Eq. (1.50) in Eq. (1.48) we get:

$$\varepsilon^{corr(1)} = Z^T B(O) + Q(O) \qquad (1.51)$$

The above equation for first order energy derivative is independent of wave function derivative. Thus, one has to solve only one extra set of perturbation independent amplitudes, i.e. the Z-vectors, defined by Eq. (1.50), in addition to the cluster amplitudes, making the procedure of obtaining first derivatives of energy more efficient.

The Z-vector technique adroitly eliminates the cumbersome evaluation of $T^{(1)}$ for first derivative of energy. Extension of the technique for higher energy derivatives, however, is non-trivial. The Lagrange Multiplier approach (LMA) of Jorgensen and co-workers [97, 104, 105] extends the benefits of the Z-vector technique for higher order derivatives of energy. Based on the method of Lagrange's undetermined multipliers,

LMA involves construction of Lagrangian as follows.

$$\Im = \left\langle \Phi_0 \middle| e^{-T} H e^T \middle| \Phi_0 \right\rangle + \sum_{q \neq 0} \lambda_q \left\langle \Phi_q \middle| e^{-T} H e^T \middle| \Phi_0 \right\rangle \qquad (1.52)$$

It can be seen that the first term on the right hand side of the above equation gives total electronic energy of the system. The Lagrange multipliers λ are optimized with the cluster equations as the constraint. The optimization of Lagrangian leads to equations for λ-vectors, which are same as Z-vectors. The CVA formulation transparently extends the cost-effectiveness for higher order derivatives. While the cluster operators obey $(2n+1)$-rule for energy derivatives, the λ-vectors follow $(2n+2)$-rule [158, 159].

1.14 Quasi-degenerate situations and multi-reference coupled cluster methods

Single reference coupled cluster (SRCC) method [28-37] is known to be among the most efficient tools for the treatment of electron correlation effects of closed shell molecular systems in cases where a single determinant provides a good zeroth order description. Among its many advantages, accurate treatment of dynamic electron correlation and size-extensivity are particularly important. These features have made SRCC method widely applicable for the calculation of correlation energy, molecular properties, gradients and potential energy surfaces [33-37]. The success of single reference CC method has motivated many research groups to extend the method for quasi degenerate situations with the help of higher excitations [37, 38]. However, in cases of molecular bond dissociation and open shell states, a multi-reference zeroth order description becomes essential for the treatment of non-dynamic electron correlation and dynamic correlation is taken care of by the built in exponential feature of wave operator. These methods are collectively referred to as multi-reference coupled cluster (MRCC) [39-45] methods. Existing MRCC approaches can be divided into three basic categories: Fock space (FS) [39, 40] or valance universal (VU), Hilbert space (HS) [41] or state universal (SU) and state selective (SS) [42-47] CC. The first two approaches are commonly in the class of multi-root MRCC methods, as they are built on the concept of Bloch equation based effective Hamiltonian [48, 49] acting within a model space. It is important to mention here that several methods based on SRCC have been extensively developed,

which are widely applicable in quasi-degenerate situations [50-57]. Within single reference framework, method of moments coupled cluster (MMCC) [50], coupled cluster linear response (CCLR) [51-54], equation of motion coupled cluster (EOMCC) [55-57], symmetry-adapted cluster configuration interaction (SAC-CI) [58], similarity transformed EOMCC (STEOMCC) [59, 60] and spin flip EOMCC (SF-EOMCC) [61] methods are commonly used to handle quasi degeneracy problems. Although these methods structurally differ from MRCC method in many aspects, their high accuracy, relative simplicity and cost effectiveness are important to note. In this thesis, we focus our concern mainly to the FSMRCC method.

3.2 Effective Hamiltonian formulation of FSMRCC theory:

The FSMRCC theory [62-75] is originally based on the concept of effective Hamiltonian (EH) [39, 40]. This uses a common vacuum with respect to which holes and particles are defined. These holes and particles are further classified as active and inactive ones. The model space is then constructed by a linear combination of suitably chosen (based on energetic criteria) active configurations. The contribution from the orthogonal complement of the model space is included through wave operator, which is used to construct the effective Hamiltonian. This effective Hamiltonian is diagonalized to get the contribution from the model space configurations. Although in the case of incomplete model space the equations are modified but the basic qualitative idea remains same.

The principle idea of effective Hamiltonian theory is to extract some of the eigenvalues of Hamiltonian from the whole eigenvalue spectrum. To obtain this, the configuration space is divided into model and orthogonal space, denoted as M and $M_\perp$ respectively. Let us denote the projection operator of these two mutually orthogonal spaces as P_M and Q_M respectively. The model space is chosen in such a manner that its linear combination can provide a good zeroth order description of the eigenstates, in which we are interested. In

practice, molecular orbital (MO) picture is being used to define the model space by choosing the close lying valance occupied and virtual orbitals. A given number of electrons are distributed among these orbital's to generate the model space configurations. If the model space contains all the configurations, generated by distributing the valance electrons among the entire valance orbital's in all possible ways, it is termed as complete model space (CMS), and otherwise it is an incomplete model space (IMS). Let us consider the Schrodinger equation for desired (say mth) eigenstates,

$$H_N \Psi_m = \Delta E_m \Psi_m \qquad (1.53)$$

We have used the normal ordered form of the Hamiltonian, $H_N = H - E_{HF}$ and $\Delta E_m = E_m - E_{HF}$.

Normal ordered Hamiltonian, in second quantization, is

$$H_N = \sum_{p,q} f_{pq} . \{p^+ q\} + \frac{1}{4} \sum_{p,q,r,s} W_{pqrs} \{p^+ r q^+ s\} \qquad (1.54)$$

The f_{pq} refer to appropriate parts of the Fock operator. The W_{pqrs} are antisymmetrized two electron integrals. The projection operator P_M of the model space acts on the exact eigenstates to generate the model function Ψ_m^o which is defined within the model space.

$$P_M \Psi_m = \Psi_m^o \qquad (1.55)$$

Defining a wave operator Ω, which acts only on the model space (i.e., $\Omega = \Omega P_M$) and transforms the model function into the exact eigenstates,

$$\Psi_m = \Omega \Psi_m^o \qquad (1.56)$$

We further define an operator $H_{N,eff}$ in such a way that,

$$H_{N,eff} \Psi_m^o = \Delta E_m \Psi_m^o \qquad (1.57)$$

By using the definition of Ω, P_M and with the help of Eq. (1.53), we obtain the well known generalized Bloch-Lindgren equation [35] in normal ordered form as,

$$H_N \Omega P_M = \Omega H_{N,eff} P_M \qquad (1.58)$$

The Bloch projection approach to solve the above equation involves left projection of P_M and Q_M leading to,

$$Q_M (H_N \Omega - \Omega H_{N,eff}) P_M = 0 \qquad (1.58)$$

$$P_M (H_N \Omega - \Omega H_{N,eff}) P_M = 0 \qquad (1.59)$$

To solve the above equations an additional normalization condition is imposed to fix $P_M \Omega P_M$ by parameterization of Ω. Usually this is employed by imposing the intermediate normalization condition $P_M \Omega P_M = P_M$ especially to the CMS. In general, the set of equations for Ω and $H_{N,eff}$ are coupled to each other through Eqs. (1.58) and (1.59) and in general $H_{N,eff}$ cannot be expressed explicitly in terms of Ω. However, when intermediate normalization is imposed, $H_{N,eff}$ can directly be written as a function of Ω. In this case Eq. (1.59) can be written as,

$$P_M H_N \Omega P_M = P_M H_{N,eff} P_M \qquad (1.60)$$

After solving the equations for Ω and $H_{N,eff}$, diagonalization of $H_{N,eff}$ within the model space provides the desired eigenvalues as,

$$H_{N,eff} C = CE \qquad (1.61)$$

$$\tilde{C} H_{N,eff} = E\tilde{C} \qquad (1.62)$$

$$\tilde{C}C = C\tilde{C} = 1 \qquad (1.63)$$

Where C ($\tilde{C}$) is the square matrix of dimension P_M, containing the columns (rows) of right (left) eigenvectors of $H_{N,eff}$ and E is the diagonal eigenvalue matrix.

In the Fock space or valance universal MRCC approach Ω is defined as,

$$\Omega = \{e^{\tilde{S}^{(k,l)}}\}P_M \tag{1.64}$$

Where { } denotes the normal product form of expansion as defined by Lindgren [64]. In this formulation Ω is valance universal which means that same Ω solves all the sectors. Its cluster structure can be written as,

$$\tilde{S}^{(i,j)} = \sum_{i=0}^{i=m} \sum_{j=0}^{j=n} S^{(i,j)} \tag{1.65}$$

Where, $S^{(i,j)}$ is the cluster operator and normal ordering is defined with respect to vacuum Φ. The maximum number of valence particles and holes in Φ are denoted by m and n, respectively. The cluster operators $S^{(i,j)}$ induces hole-particle excitations out of each of model spaces $P^{(i,j)}$ containing i valance particle and j valance hole with respect to Φ. The cluster operators $S^{(i,j)}$ contain i valance particle and j valance hole destruction operator. Contraction between different cluster operators is avoided due to normal ordering leading to partial hierarchical decoupling referred to as sub system embedding condition (SEC) [62].

For simplicity, here onwards, we will denote the cluster operator of (0, 0) sector, $S^{(0,0)}$ as $T^{(0,0)}$ or sometimes simply as T. The final working equation for FSMRCC for CMS (and some of the special IMS) can be written as,

$$Q_M(\overline{H}_N\{e^S\} - \{e^S\}H_{N,eff})P_M = 0 \tag{1.66}$$

$$H_{N,eff} = P_M\overline{H}_N\{e^S\}P_M \tag{1.67}$$

1.16 Intruder state problem and Intermediate Hamiltonian formulation of FSMRCC

The FSMRCC method [62-75] has been successfully used for difference energy calculations. However, in several cases when model space is increased in order to target more excited states, the method faces convergence difficulties. This is termed as intruder state [76, 77] problem. The intermediate Hamiltonian [78] formulation of FSMRCC (IHFSMRCC) [79-88] method provides a more efficient and reliable as well as numerically stable way to handle the intruder state problem. Intruder state problem can also be avoided by using SSMRCC methods. Among few variants of SSMRCC method in literature are Brillouin-Wigner (BW) MRCC [42, 43] ansatz, exponential MR wave function ansatz (MRexpT) [44], the state- specific MRCC method suggested by Mukherjee and coworkers (Mk-MRCC) [45] and internally contracted MRCC (ic-MRCC) [46] theory. Recently, Nooijen and co-workers proposed multi-reference EOMCC (MR-EOMCC) [47] theory.

The idea of intermediate Hamiltonian was first introduced by Malrieu [78] *et al* in the context of degenerate perturbation theory. The basic idea of IH formulation is to divide the configuration space into three subspaces namely main, intermediate and outer space with the projection operators P_M, P_I and Q_o respectively [78]. The intermediate space is imposed as a buffer between main and outer space. This intermediate space can be defined formally in terms of excitation level of highest sector cluster operators which defines the FSMRCC equations. The main space of IH formulation is same as the model space of effective Hamiltonian theory, while the intermediate space (P_I) has been obtained from the complementary space (Q_M) of EH theory by further dividing it into two parts: the intermediate and the outer space. Diagonalization of intermediate Hamiltonian provides the eigenvalues from which only a subset of roots, corresponding to main space, are equivalent to those obtained through effective Hamiltonian theory. Various kinds of intermediate Hamiltonian

schemes have been developed and implemented by several workers. Meissner has applied the intermediate Hamiltonian technique to reformulate the FSCC method for excitation energy [79-81]. The eigenvalue-independent-partitioning (EIP) [89] technique by Sinha *et al* can also be treated as a specific implementation of intermediate Hamiltonian in Fock space. The IH formulation of FSMRCC, which leads to a completely new method, has been developed and extensively applied by Kaldor and coworkers [90, 91]. In this thesis work, we have particularly chosen the IHFSMRCC formulation of Meissner for our further considerations, which will be discussed in detail in chapter 3 of this thesis.

1.17 Molecular response properties through effective Hamiltonian based FSMRCC

Formulation of efficient theoretical as well computational technique for the evaluation of molecular properties in FSMRCC method is quite desirable in order to increase the scope and applicability of the method. The linear response in effective Hamiltonian based FSMRCC method was initiated by Pal [92] and then implemented by Pal and coworkers for the first order properties [93, 94]. Ajitha and Pal developed the Z-vector like formalism in FSMRCC [102, 103] framework, which eliminated the highest sector cluster response quantities.

As we have already discussed, molecular response properties are basically governed by the derivative of energy with respect to external perturbation. The energy derivatives can be most easily obtained by using the Lagrange multiplier approach, which is based on Lagrange method of undetermined multipliers. In this method we define a functional ($\Im$, a scalar quantity), which consist a explicit energy expression along with equations that define all the quantities appearing in the energy expression, each multiplied by an undetermined parameter. After making the functional stationary with respect to Lagrangian multipliers, cluster amplitudes determining equations are obtained, which are already satisfied due to energy equations. Making the functional

stationary with respect to cluster amplitudes, leads to the linear equations which determine the Lagrangian multipliers. The Lagrangian functional is defined for a specific eigenstate. When the stationary conditions are satisfied, the energy derivatives with respect to external perturbation can be directly obtained in terms of Hamiltonian matrix derivatives along with the cluster amplitudes and Lagrange multipliers. In this way the evaluation of cluster amplitude derivatives for each mode of perturbation can be eliminated at the expense of solving a linear equation in Lagrange multiplier, which are independent of external perturbation. This hierarchy can be extended for the higher order energy derivatives which leads to (2n+1) and (2n+2) rules for cluster amplitudes and Lagrange multipliers respectively. This means that (2n+1)th and (2n+2)th order energy derivatives can be obtained only with the knowledge of up to nth order derivatives of cluster amplitudes and Lagrangian multipliers respectively. We have briefly discussed the LMA in the context of SRCC method in section 1.12

The extension of Lagrange multiplier approach in FSMRCC theory using complete model space for the first order energy derivatives was initiated by Szalay [104]. This approach was further generalized for general incomplete model space by Shamasundar et al. [105, 106] for higher order energy derivatives and also implemented by Pal and coworkers [107-110].

We will discuss about LMA and molecular response properties especially in context to effective vs. intermediate Hamiltonian formulation of FSMRCC theory in chapter 3 in detail, which will illustrate the significance of the work presented in this thesis.

1.18 Scope and objective of the thesis

As mentioned earlier, the traditional effective Hamiltonian based FSMRCC theory suffers from intruder states. The intermediate Hamiltonian formulation of FSMRCC provides an alternative way to reach the convergence in a more efficient manner with larger model space. This not only helps one to obtain

more number of states, but also, in several cases, significantly improves the correlation effects. Apart from these advantages, a considerable amount of computational simplicity arises. Hence in our opinion, it is desirable to extend the LMA [97, 104, 105] in IHFSMRCC formulation of Meissner [79] for energy derivatives, in order to obtain excited state properties for desired number of states with bigger basis sets and larger model space in numerically stable and cost effective way. The same is one of the most prominent objectives of this thesis. Apart from IHFSMRCC, a single reference variant of variational coupled cluster i.e. extended coupled cluster (ECC) has also been explored for ground state molecular response properties.

The present thesis is organized as follows. In chapter 2, we discuss the extended coupled cluster through nth perturbation order for ground state molecular response properties at equilibrium as well as stretched geometry for closed shell molecular system. In chapter 3, LMA has been applied in IHFSMRCC framework to derive expressions up to 2nd order energy derivatives. In chapter 4, LMA-IHFSMRCC formulation has been applied for electronic transition dipole moment and oscillator strength of closed shell molecular systems. Chapter 5 is dedicated to the application of IHFSMRCC theory for the calculation of core excitation energy.

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Chapter 2

Extended coupled cluster through nth perturbation order for molecular response properties: A comparative study

In this chapter, we have presented and analyzed the extended coupled cluster (ECC) energy functional, truncated up to nth perturbation order limit to operators of the single and double excitations. The expression for the first order energy derivatives based on the above truncation schemes has been derived and numerically analyzed. We have done a comparative study for dipole moment in various perturbative ECC (n) methods ($2 \leq n \leq 5$) for three systems (HF, H_2O and BH) at equilibrium geometry. We have particularly studied two variants of ECC (4) and ECC (5*) method for stretched geometry. We have analyzed the contribution of important terms present in ECC functional based on perturbative argument. We have compared our results with standard coupled cluster (CCSD) as well as cubic truncated ECC and also benchmarked with the full CI results wherever available.

2.1 Introduction:

In chapter 1, we have briefly discussed the general overview of the electronic structure theory and evaluation of molecular properties through linear response approach for ground as well as excited states of atomic and molecular systems. In this chapter, we will present and implement a variational variant of single reference coupled cluster method for molecular response properties.

Over the past few decades, coupled cluster methods [1-4] have been established as promising tools for evaluation of correlation energy as well as molecular properties. It introduces the dynamic correlation in efficient way through infinite partial summation of important terms of many body perturbation theories. Multi-reference variants of this method have also been developed for excitation energy as well as properties for open and closed shell molecules [5-12].

The linear response approach to the coupled cluster method was originally formulated by Monkhorst [13] and further developed and applied with orbital relaxation built in by Bartlett and coworkers, who introduced the Z-vector [14] technique within the coupled cluster (CC) framework [15] to simplify the energy derivative problem. With the help of Z vector method, energy derivative for each mode of perturbation can be obtained by solving only an additional linear equation, which contains one extra set of perturbation-independent parameters. This algebraic method is however quite laborious and more difficult for higher order derivatives. Jorgensen and coworkers [16] formulated constrained variational approach based on method of Lagrange multipliers. The final equation is shown to be equivalent as the ones obtained through Z vector technique, but this approach is found to be suitable for extension to progressive higher order derivatives.

Parallel to these developments, Pal et al [17-19] also pursued a fully stationary approach to expectation value coupled cluster (XCC). It has been realized that variational methods are quite desirable especially for molecular properties because of its fulfillment of GHF theorem and (2n+1) rule. Pal and coworkers

implemented the variational method which is based on direct variation of suitable energy functional without any constraint [17]. Various forms of energy functional like expectation value (XCC) [17-20], Unitary coupled cluster (UCC) [21, 22] and extended coupled cluster (ECC) [23, 24] have been studied in literature. Among these ECC has shown to be most promising as well as successful functional in particular for properties. Due to full exponential parameterization of de-excitation operator, ECC functional includes terms which are nonlinear in de-excitation amplitudes, in addition to the terms present in normal CC functional. These additional non linear terms lead to coupling between left and right eigenvector equations.

The idea of ECC functional was first developed by Arponen [23] and then used by Arponen and coworkers [24] in the context of condensed matter physics. ECC functional was later used to develop a consistent superoperator resolved theory by Mukherjee and coworkers [25]. Among its many advantageous features, double linked structure of ECC functional is a particular one, which not only ensures a naturally terminating series of energy functional, but also provides a fully connected set of stationary equations for cluster amplitudes even in its approximate versions.

The ECC functional contains the set of de-excitation amplitudes, whose number is same as that of excitation amplitudes. Due to the presence of additional de-excitation operator in ECC functional in compare to standard or normal CC (NCC) functional, twice the number of variables has to be solved in a coupled manner and hence ECC method is computationally more expansive than normal CC method. A decoupled approximation of ECC method has been formulated by Vaval [26] which simplifies the problem. However, this decoupling scheme leads to loss in accuracy.

Although ECC functional has naturally terminating series due to its double linking structure, natural truncation occurs at very high powers in excitation and de-excitation amplitudes. Hence its efficient implementation through diagrammatic

techniques requires the large number of diagrams to be coded. The situation is more challenging because of the fact that some of the diagrams of the term $\left\langle \Phi_{ij}^{ab} \left| \Sigma_2'^2 H_N \Sigma_2^4 \right| \Phi_0 \right\rangle$ contributing to the Σ_2' amplitude equations scale as M^{10} after proper factorization, even in its approximate version with full singles and doubles (ECCSD) [27]. This prohibits its wider application to quite sizeable systems. Inclusion of higher excitation connected clusters like triples Σ_3 in ECC functional is computationally even more demanding. Hence ECC functional with singles and doubles requires further approximations to be imposed in order to make it computationally feasible for its larger application. Various forms of approximation schemes has already been implemented and analyzed by several workers [28-30].

A perturbation based analysis generally provides a guideline to identify the importance of individual terms in energy functional. The different variations of UCC and XCC functional known as XCC(n)/UCC(n) have been used for energy calculations by Bartlett and coworkers [20, 21]. These functionals contain all the terms correct through a given order n. Similar kind of perturbation based functional for ECC (n) has also been used and analyzed by Kucharaski and Bartlett [31] for correlation energy at the equilibrium as well as stretched geometry.

In this chapter we have presented and analyzed the ECC functional correct up to nth perturbation order with singles and doubles approximation for the first order molecular response properties. We have done a comparative study for dipole moment in various ECC (n) methods ($2 \leq n \leq 5$) for three systems (HF, H_2O and BH) at equilibrium geometry. We have also proposed an approximate version of ECC (5), which will be computationally simpler than the exact ECC (5). We have denoted this approximation scheme as ECC (5*). We found the performance of ECC (4) and ECC (5*) to be optimum among all at least at the equilibrium geometry. We have further tested its efficiency at stretched geometries and analyzed the contribution of important terms present in ECC functional based on

perturbative argument. We have compared our results with cubic truncated ECC as well as standard Coupled Cluster methods. Also we have benchmarked our results with the full CI, wherever feasible.

This chapter is organized as follows. Sec. 2.2 gives the brief overview of the theory of ECC functional. Sec. 2.3 presents explicit working equation for ECC functional for different perturbation orders. Sec. 2.4 contains the results and discussion pointing to the significance of this work. Sec. 2.5 provides some concluding remarks and future directions.

2.2 Theory of ECC functional and analytical derivative:

The concept of bi-orthogonal CC functional, also termed as ECC functional, is derived by Arponen [23] and applied by Arponen and their coworkers in condensed matter [24]. The ECC functional based on double similarity transformation uses different Ket and conjugate vectors.

$$\langle H \rangle = \langle \Psi' | H | \Psi \rangle \tag{2.1}$$

Where, Ψ and Ψ' are parameterized differently and are bi-orthogonal to each other,

$$|\Psi\rangle = \exp(T)|\Phi_0\rangle \tag{2.2a}$$

$$\langle \Psi'| = \langle \Phi_0 | \exp(\Sigma') \exp(-T) \tag{2.2b}$$

Where,

$$T = \sum_k t_k C_k^+ \tag{2.3a}$$

$$\Sigma' = \sum_k \sigma'_k C_k \tag{2.3b}$$

Where C_k^+ are different hole-particle creation operators and the C_k are the conjugates of C_k^+ operators. t_k and σ'_k are the corresponding coefficients. As Σ' is a de-excitation operator, $\Sigma'|\Phi_0\rangle = 0$ Ket vector may be written as

$$|\Psi\rangle = \exp(T).\exp(\Sigma')|\Phi_0\rangle \tag{2.4}$$

The average value functional of the Hamiltonian H is given by

$$\langle \Psi' | H | \Psi \rangle = \langle \Phi_0 | e^{\Sigma'} e^{-T} H e^{T} e^{-\Sigma'} | \Phi_0 \rangle$$

$$= \langle \Phi_0 | \overline{H} | \Phi_0 \rangle$$

(2.5)

Where, $\overline{H}$ is a double similarity transformed operator. Arponen and coworkers introduced a new set of operators Σ and Σ' by transforming T and Σ' as below to arrive at a more convenient form of the functional.

$$\Sigma | \Phi_0 \rangle = 1 - | \Phi_0 \rangle \langle \Phi_0 | e^{\Sigma'} T | \Phi_0 \rangle \ \& \ \Sigma = \sum_k \sigma_k C_k^+$$

(2.6a)

The amplitude of $\Sigma_1 \{\sigma_k\}$ may be defined as

$$\sigma_k = \langle \Phi_0 | C_k e^{\Sigma'} T | \Phi_0 \rangle$$

(2.6b)

Using the above operators Σ and Σ' the functional may be written as,

$$E = \langle \Phi_0 | e^{\Sigma'} e^{-\Sigma} H e^{\Sigma} e^{-\Sigma'} | \Phi_0 \rangle_{DL}$$

$$= \langle \Phi_0 | e^{\Sigma'} (He^{\Sigma})_L | \Phi_0 \rangle_{DL}$$

(2.7)

Where, L denotes that Σ' operators to the right of H are linked and DL indicates double linking, i.e. the Σ' operator must either be connected to H or to at least two different Σ vertices.

The amplitudes of Σ and $\Sigma'(\sigma_k$ and $\sigma_k')$ are obtained by the solution of a stationary set of equations,

$$\delta E / \delta \Sigma = 0$$

(2.8a)

$$\delta E / \delta \Sigma' = 0$$

(2.8b)

Eqs (2.8a) and (2.8b) have to be solved in coupled way.

The expression $\delta E / \delta \Sigma$ and $\delta E / \delta \Sigma'$ may be obtained diagrammatically by systematically deleting Σ and Σ' vertices from the diagrams of energy in all possible way.

Because of the fulfillment of Generalized Hellmann-Feynman theorem (GHF) [43, 44], first order energy derivative may be simply obtained by replacing H with $H^{(1)}$, where $H^{(1)}$ is the first order Hamiltonian derivative.

$$E^{(1)} = \left\langle \Phi_0 \left| e^{\Sigma'} (H^{(1)} e^{\Sigma})_L \right| \Phi_0 \right\rangle_{DL} \tag{2.9}$$

Where,

$$H^{(1)} = F^{(1)} + V^{(1)} = [dH(\lambda)/d\lambda]_{\lambda=0}$$

$$= \Sigma f_{pq}^{(1)} . \{p^+ q\} + 1/4 \Sigma < pq || rs >^{(1)} . \{p^+ q^+ sr\}$$

$$\tag{2.10}$$

where $F^{(1)}$ and $V^{(1)}$ are the one and two body Hamiltonian derivatives respectively and p, q, r and s are the molecular orbital's. In order to get the first order Hamiltonian derivatives ($F^{(1)}$ and $V^{(1)}$), one and two electron part of Hamiltonian in AO basis along with MO coefficient and the MO coefficient derivatives are required. MO coefficient derivatives may be obtained by solving the coupled perturbed Hartree Fock (CPHF) equation. The detailed procedure and working equations are well described at several places [32, 33]. If a linearized form in de-excitation operator is used for conjugate vector, standard non variational CC equations can be obtained from the stationarity of ECC functional. Under this linearized, approximation excitation amplitude are decoupled from de excitation amplitude equations.

One major drawback of ECC functional is that due to presence of nonlinear terms in de-excitation operators, left and right vectors are coupled to each other and hence the equations for σ and σ' amplitudes have to be solved in coupled iterative manner, which doubles the number of variables compare to NCC functional. Though double similarity ensures the natural termination of the ECC functional, it terminates at a high order in Σ and Σ' amplitudes, even in its most approximate version with singles and doubles (ECCSD). Hence it is essential to impose further approximations to ECC functional to make it computationally feasible for its practical application.

There are many approximation schemes developed and applied by several authors. Van Voorhis et al. [28] used an approximation in which ECC functional has been truncated up to quadratic terms in both the excitation and de-excitation operators.

Piecuch and coworkers [29, 30] developed an approximation scheme termed as quadratic coupled cluster (QCC). In QCC de-excitation operator has been approximated up to quadratic terms. Pal and coworkers developed and extensively used ECC functional for electric [33-36] as well as magnetic properties [37, 38], in which energy functional has been truncated up to cubic power in excitation and de excitation operators.

2.3 ECC functional through nth perturbation order:

A perturbation based analysis may provide several approximation schemes in which ECC functional may be truncated up to a given order of perturbation theory. It may be defined as ECC (n), where n indicates the order of terms whose leading contributions are n^{th} order in the correlation energy, but due to infinite order character of cluster amplitudes, selective infinite order corrections will also be included. In the next subsections we will present the hierarchy of ECC (n) methods ($2 \leq n \leq 5$) for the first order molecular response properties. We have taken canonical HF as our reference for simplicity. We have further defined the additional approximations as ECCSD (n), which means to restrict the ECC (n) equations within singles and doubles in excitation as well as de-excitation operators. For the sake of brevity we will entirely drop the symbol SD from our notation and denote the ECCSD (n) as ECC (n) in future.

2.3.1 ECC (2)

Starting from the canonical HF as a reference, T_2 and V_N appear in first order, while T_1 occurs in second order and F_N is zeroth order in correlation. Putting these definitions in Eq. (2.7) and expanding all the terms up to second order in correlation energy we obtain,

$$\Delta E_{ECC(2)} = \left\langle \Phi_0 \left| [(V_N \Sigma_2)_C + (\Sigma_2' V_N)_C + \Sigma_2'(F_N \Sigma_2)_C] \right| \Phi_0 \right\rangle_{DL} \tag{2.11}$$

where Σ_2 and Σ_2' are defined by following equations,

$$0 = \left\langle \Phi_{ij}^{ab} \left| [V_N + (F_N \, \Sigma_2)_C] \right| \Phi_0 \right\rangle \tag{2.12a}$$

$$0 = \left\langle \Phi_0 \left| [V_N + (\Sigma_2' F_N)_C] \right| \Phi_{ij}^{ab} \right\rangle \tag{2.12b}$$

Finally, correlation energy is given by,

$$\Delta E_{ECC(2)} = \left\langle \Phi_0 \left| (V_N \, \Sigma_2)_C \right| \Phi_0 \right\rangle \tag{2.13}$$

which is same as the equations determining the MBPT (2) method. This shows that MBPT (2) satisfies the GHF theorem. Hence the correlation energy derivative $\Delta E^{(1)}$ may be written as,

$$\Delta E_{ECC(2)}^{(1)} = \left\langle \Phi_0 \left| (V_N^{(1)} \, \Sigma_2)_C + (\Sigma_2' \, V_N^{(1)})_C + \Sigma_2' (F_N^{(1)} \, \Sigma_2)_C] \right| \Phi_0 \right\rangle_{DL} \tag{2.14}$$

2.3.2 ECC (3)

Similarly the correlation energy for ECC (3) functional is given by,

$$\Delta E_{ECC(3)} = \Delta E_{ECC(2)} + \left\langle \Phi_0 \left| \Sigma_2' (V_N \, \Sigma_2)_C \right| \Phi_0 \right\rangle_{DL} \tag{2.15}$$

Where,

$$0 = \left\langle \Phi_{ij}^{ab} \left| [V_N + (F_N \, \Sigma_2)_C + (V_N \, \Sigma_2)_C] \right| \Phi_0 \right\rangle \tag{2.16a}$$

$$0 = \left\langle \Phi_0 \left| [V_N + (\Sigma_2' \, F_N)_C + (\Sigma_2' \, V_N)_C] \right| \Phi_{ij}^{ab} \right\rangle \tag{2.16b}$$

When the above equations are satisfied the correlation energy is given by the same above Eq. (2.13) The above Eqs are same as that of LCCD method, which means that LCCD satisfies the GHF theorem and the correlation energy derivative may be written as,

$$\Delta E_{ECC(3)}^{(1)} = \Delta E_{ECC(2)}^{(1)} + \left\langle \Phi_0 \left| \Sigma_2' (V_N^{(1)} \, \Sigma_2)_C \right| \Phi_0 \right\rangle_{DL} \tag{2.17}$$

2.3.3 ECC (4)

Including all the possible terms of eq. 7 up to 4th order in correlation energy, we obtain,

$$\Delta E_{ECC(4)} = \Delta E_{ECC(3)} + \left\langle \Phi_0 \middle| \Sigma_1'(V_N \Sigma_2)_C + \Sigma_2'(V_N \Sigma_1)_C \right.$$
$$\left. + \Sigma_1'(F_N \Sigma_1)_C + \Sigma_2'(V_N \Sigma_2^2)_C / 2 \middle| \Phi_0 \right\rangle_{DL} \tag{2.18}$$

Where,

$$0 = \left\langle \Phi_0 \middle| [V_N + (\Sigma_2' F_N)_C + (\Sigma_2' V_N)_C + (\Sigma_1' V_N)_C + \Sigma_2'(V_N \Sigma_2)_C] \middle| \Phi_{ij}^{ab} \right\rangle \tag{2.19a}$$

$$0 = \left\langle \Phi_0 \middle| [(\Sigma_2' V_N)_C + (\Sigma_1' F_N)_C] \middle| \Phi_i^a \right\rangle \tag{2.19b}$$

$$0 = \left\langle \Phi_{ij}^{ab} \middle| [V_N + (F_N \Sigma_2)_C + (V_N \Sigma_2)_C + (V_N \Sigma_2^2)_C / 2] \middle| \Phi_0 \right\rangle \tag{2.19c}$$

$$0 = \left\langle \Phi_i^a \middle| [(F_N \Sigma_1)_C + (V_N \Sigma_2)_C] \middle| \Phi_0 \right\rangle \tag{2.19d}$$

The final correlation energy is still given by the Eq. (2.12) The correlation energy derivative is given by,

$$\Delta E_{ECC(4)}^{(1)} = \Delta E_{ECC(3)}^{(1)} + \left\langle \Phi_0 \middle| [\Sigma_1'(V_N^{(1)} \Sigma_2)_C + \Sigma_2'(V_N^{(1)} \Sigma_1)_C \right.$$
$$\left. + \Sigma_1'(F_N^{(1)} \Sigma_1)_C + \Sigma_2'(V_N^{(1)} \Sigma_2^2)_C / 2] \middle| \Phi_0 \right\rangle_{DL} \tag{2.20}$$

In ECC (4) framework, energy functional is correct at least up to 4th order in correlation, hence, T$_1$ amplitudes are correct up to second order in correlation. It is a well established fact that the leading contribution to the dipole moment is given by the terms $F_N^{(1)} T_1$, thus we can conclude that the dipole moment obtained through ECC (4) is correct up to 2nd order in correlation with singles and doubles only approximation.

2.3.4 ECC (5*)

An obvious next step towards the hierarchy of ECC (n) methods for n=5 is ECC (5). This functional, which is correct up to 5th order in correlation energy with singles and doubles, is given by,

$$\Delta E_{ECC(5)} = \Delta E_{ECC(4)} + \left\langle \Phi_0 \middle| [\Sigma_1'(V_N \Sigma_1)_C + \Sigma_2'(V_N \Sigma_1 \Sigma_2)_C + \Sigma_1' \Sigma_2'(V_N \Sigma_2)_C \right.$$
$$\left. + (\Sigma_1'^2 V_N) + (V_N \Sigma_1^2 / 2)_C + \{\Sigma_2'^2(V_N \Sigma_2^2)_C\} / 4] \middle| \Phi_0 \right\rangle_{DL} \tag{2.21}$$

It is important to note that the ECC (5) functional involves the term $(\Sigma_2'^2 V_N \Sigma_2^2)/4$. This only term requires huge effort of coding in its implementation through diagrammatic technique. Therefore, we require some other suitable way of approximations to be applied to ECC functional to avoid this quartic term while, at the same time improving the correlation energy beyond ECC (4). In fact it may be quite interesting to see the qualitative reasoning as well as numerical validity of such an approximation schemes. As we have already seen in previous subsections that Σ_1 and Σ_1' amplitudes evaluated in ECC (4) scheme are correct only up to second order in correlation, we may include some more terms in ECC (4) functional in order to make the Σ_1 and Σ_2 (as well as Σ_1' and Σ_2') equations correct up to third order. The terms present in Σ_1 and Σ_2 amplitude equations are present in fifth and fourth order respectively in correlation energy functional. Some of the special terms like $\Sigma_2' V_N \Sigma_1 \Sigma_2$ which are appearing in third order in Σ_1 equations are present in fifth order in correlation energy functional, hence we are forced to include such terms in Σ_2 equations despite its appearance in 4th order. With this approximation scheme we lead to ECC functional which is correct up 5th order in correlation except for the term $(\Sigma_2'^2 V_N \Sigma_2^2)/4$ which, we have denoted by ECC (5*).

$$\Delta E_{ECC(5^*)} = \Delta E_{ECC(5)} - \left\langle \Phi_0 \left| \Sigma_2'^2 (V_N \Sigma_2^2)_C / 4] \right| \Phi_0 \right\rangle_{DL} \tag{2.22}$$

In our opinion the best possible theoretical justification for dropping the above quartic term may be given as follows. As we know that the term $(\Sigma_2'^2 V_N \Sigma_2^2)/4$ present in ECC (5) can contribute to the Σ_2 (and Σ_2') equations in 4th order. This Σ_2 will affect the Σ_1 equations in 5th order and hence this term can contribute to the dipole moment through $F_N^{(1)} T_1$ at 5th order in correlation. As we have already seen that the dipole moment obtained through ECC (4) is correct only up to second order, we should worry about the 5th order contribution of the above quartic term,

56

before taking care of 3rd and 4th order contribution of dipole moment.

Making the ECC (5*) functional stationary with respect to Σ_2 and Σ_2' amplitudes, we get following set of equations,

$$0 = \left\langle \Phi_{ij}^{ab} \left| [V_N + (F_N \Sigma_2)_C + (V_N \Sigma_2)_C + \{(V_N \Sigma_2^2)_C / 2\} \right. \right.$$
$$\left. \left. + (V_N \Sigma_1)_C + (V_N \Sigma_1 \Sigma_2)_C + \Sigma_1'(V_N \Sigma_2)_C] \right| \Phi_0 \right\rangle_C \tag{2.23a}$$

$$0 = \left\langle \Phi_i^a \left| (F_N \Sigma_1)_C + (V_N \Sigma_1)_C + (V_N \Sigma_2)_C + \Sigma_2'(V_N \Sigma_2)_C + (\Sigma_1' V_N)_C \right| \Phi_0 \right\rangle_C \tag{2.23b}$$

$$0 = \left\langle \Phi_0 \left| [V_N + (\Sigma_2' F_N)_C + (\Sigma_2' V_N)_C + (\Sigma_1' V_N)_C + \Sigma_2'(V_N \Sigma_1)_C \right. \right.$$
$$\left. \left. + \Sigma_2'(V_N \Sigma_2)_C + (\Sigma_1' \Sigma_2' V_N)_C + (\Sigma_1' V_N)_C] \right| \Phi_{ij}^{ab} \right\rangle_C \tag{2.23c}$$

$$0 = \left\langle \Phi_0 \left| (\Sigma_2' V_N)_C + \Sigma_2'(V_N \Sigma_2)_C + (\Sigma_1' F_N)_C + (\Sigma_1' V_N)_C + (V_N \Sigma_1)_C \right| \Phi_i^a \right\rangle_C \tag{2.23d}$$

The correlation energy derivative, $\Delta E^{(1)}$ is given by,

$$\Delta E_{ECC(5')}^{(1)} = \Delta E_{ECC(4)}^{(1)} + \left\langle \Phi_0 \left| [\Sigma_1'(V_N^{(1)} \Sigma_1)_C + \Sigma_2'(V_N^{(1)} \Sigma_1 \Sigma_2)_C + \Sigma_1' \Sigma_2'(V_N^{(1)} \Sigma_2)_C \right. \right.$$
$$\left. \left. + (\Sigma_1'^2 V_N^{(1)}) + (V_N^{(1)} \Sigma_1^2 /2)_C + \Sigma_2'(F_N^{(1)} \Sigma_1 \Sigma_2)_C] \right| \Phi_0 \right\rangle_{DL} \tag{2.24}$$

2.4 Results and discussions:

In this section, we present the results of first order energy derivatives i.e. dipole moments of three test systems HF, H_2O and BH molecules. In the first subsection we present and analyze the result of dipole moment of these three systems at equilibrium geometry. Comparative analyses of these values provide us a way to optimize the ECC (n) methods with n=4 and 5.

In the next subsections, we present and study the results of dipole moment of the above used molecules in the same basis set, but at stretched geometry. We choose only those ECC (n) methods for dipole moment surface which have the optimum performance at least at equilibrium geometry. We analyze the dipole moment surface of the above molecules on the basis of the perturbation order of the leading

terms in energy derivatives. We have chosen two basis sets for each of the three systems. For the HF molecule, Double zeta (DZ) [39] and aug-cc-pVQZ basis sets, for the BH molecule, DZP [40] and aug-cc-pVTZ basis and for the Water molecule, DZ and aug-cc-pVTZ basis sets have been used. The primary reason for using such a small basis sets like DZ and DZP is the feasibility of full CI calculation in these basis sets without any frozen orbital's using GAMESS package. In our entire calculations, equilibrium geometry (Re) of the three test systems HF, BH and H_2O is as follows. The bond length of HF, BH and H_2O molecule is kept 1.732, 2.239 and 1.809 a.u. respectively and the H-O-H bond angle in water is 104.52. In case of symmetrical stretching of water, H-O-H bond angle is kept fixed and same as 104.52.

2.4.1   ECC (n) at equilibrium geometry:

ECC (n) results for the HF molecule, at the equilibrium geometry for 2≤n≤5 are presented in Table 2.1. We have performed each calculation in two basis sets. For the purpose of benchmarking of ECC (n) methods with full CI, DZ basis has been chosen. Subsequently, ECC calculations have been performed in significantly bigger basis i.e. aug-cc-pVQZ.

We observe from the Tables that energy and dipole moment progressively improve from ECC (2) to ECC (4) towards the full CI energy for all the three systems (HF, BH and water). As we see from Table 2.1 that the NCC energy as well as dipole moment values are very close to full CI, we compared our ECC (n) results with NCC values in Table 2.2 in case of bigger basis set calculation, where full CI values are not available. Both energy as well as dipole moment saturate at ECC (4) level.

Table 2.1

Dipole values of three test systems through ECC (n) methods at equilibrium geometry benchmarked with full CI (in a. u.).

System (basis)		RHF	ECC(2)	ECC(3)	ECC(4)	ECC(5*)	Cubic-ECC	NCCSD	Full CI
HF(DZ)	E	100.020	100.152	100.154	100.152	100.155	100.154	100.157	100.163
	μ	0.935	0.907	0.897	0.899	0.899	0.899	0.899	0.897
H_2O(DZ)	E	76.0093	76.1472	76.1533	76.1541	76.1539	76.1539	76.1540	76.1557
	μ	1.055	1.029	1.018	1.020	1.020	1.021	1.020	1.017
BH(DZP)	E	25.1239	25.1942	25.2238	25.2198	25.2201	25.2199	25.2200	25.2216
	μ	0.777	0.715	0.548	0.601	0.599	0.600	0.600	0.594

Table 2.2

Dipole values of three test systems through ECC (n) methods at equilibrium geometry in bigger basis set calculation (in a. u.).

System (basis)		SCF	ECC(2)	ECC(3)	ECC(4)	ECC(5*)	Cubic ECC	NCCSD
HF(aug-cc-pVQZ)	E	100.0690	100.4102	100.4130	100.4099	100.4096	100.4095	100.4097
	μ	0.755	0.711	0.713	0.714	0.716	0.716	0.714
H_2O(aug-cc-pVTZ)	E	76.0611	76.3519	76.3608	76.3567	76.3565	76.3564	76.3566
	μ	0.777	0.726	0.729	0.730	0.732	0.732	0.730
BH(aug-cc-pVTZ)	E	25.1303	25.2187	25.2495	25.2434	25.2436	25.2435	25.2436
	μ	0.685	0.633	0.507	0.556	0.555	0.555	0.556

In case of HF and H_2O, dipole moment values for ECC (3) are also very close to full CI as well as NCC values, but for the case of BH molecule although energy is reasonably closer to full CI and NCC, its dipole moment values differ significantly. This observation is related to the fact that the leading contribution of

correlation is governed by Σ_2 amplitudes through $V_N \Sigma_2$ term, while dipole moment is controlled by Σ_1 amplitudes through $F_N^{(1)} \Sigma_1$ term. In case of ECC (3), Σ_2 amplitudes obtained are correct up to second order, while at the same time Σ_1 does not appear at all in energy functional and hence dipole moment obtained through ECC (3) energy functional is not correct up to any particular order. Even a single example of BH molecule is sufficient to discard the possibility of ECC (3) as a method for evaluating the dipole moment. In table 2.1 ECC (4), ECC (5*), cubic-ECC and NCC dipole moment values are almost identical to each other and very close to their corresponding full CI values (within the range of ± 0.007 a.u.). We find both of the ECC (4) and ECC (5*) methods to be optimum and suitable for evaluation of dipole moment among the ECC (n) (2≤n≤5) methods. As for as relative performance of ECC (5*) over ECC (4) is concerned, ECC (5*) dipole moment is observed to be slightly better than ECC (4) in case of BH only. For the case of HF and H_2O molecules, both the methods provide similar results for the bigger basis set calculation, where full CI values are not available, we find the ECC(4) dipole moment values to be closer to NCC values compare to ECC(5*) dipole values. In fact it seems to be difficult to conclude about their relative performance by a single point calculation of these three systems. We find both of these methods to be appropriate to be tested their performance as well as relative efficiency for the evaluation of dipole moment at stretched geometry.

2.4.2 ECC (n) methods at stretched geometry:

In Tables 2.3 and 2.4, we present the dipole moment values of HF, H_2O and BH molecules by ECC (4) and ECC (5*) methods but at stretched geometry (from 0.75 to 2.0 Re). In Table 2.3 calculations are performed in smaller basis (DZ and DZP) to benchmark with full CI, while in table 2.4 the same calculation is performed in significantly bigger basis (aug-ccpVTZ and aug-ccpVQZ). In both the tables we have compared our results with earlier developed Cubic truncated

ECC as well as NCC values.

2.4.2.1 HF

It is very clear from the Table 2.3 that for HF molecule in DZ basis Cubic ECC and NCC dipole values are same and equal to full CI values at 0.75 Re and 1.25 Re. ECC (5*) dipole value is 0.002 a.u. lower than ECC (4) and closer to full CI value at 1.5 Re, but beyond 1.5 Re, convergence of ECC (5*) method becomes progressively difficult. We were unable to converge the amplitude equations at and beyond 1.75 Re for ECC (5*) method. From the table 2.4 where same calculation is performed in aug-cc-pVQZ basis for which full-CI values are not available, we find our ECC (4) to be closer to the NCC than that of ECC (5*) except at 0.75 and 1.5 Re. One of the most interesting aspects of the ECC (4) method is that the dipole values obtained by this method are significantly better than the cubic truncated ECC at 2.0 Re, as is clear from both of the Table 2.3 and 2.4.

Table 2.3

Dipole values of three test systems through ECC (n) methods at stretched geometry benchmarked with full CI (in a. u.).

System (basis)	Geometry	RHF	ECC(4)	ECC(5*)	Cubic-ECC	NCCSD	Full-CI
HF (DZ)	0.75 Re	0.802	0.801	0.801	0.801	0.801	0.801
	1.00 Re	0.935	0.899	0.899	0.899	0.899	0.897
	1.25 Re	1.066	0.953	0.951	0.952	0.951	0.947
	1.50 Re	1.198	0.936	0.932	0.931	0.931	0.922
	1.75 Re	1.344	0.828	--------	0.830	0.821	0.805
	2.00 Re	1.510	0.630	--------	0.793	0.625	0.604
H_2O (DZ)	0.75 Re	0.993	0.996	0.996	0.996	0.996	0.995
	1.00 Re	1.055	1.020	1.020	1.021	1.020	1.017
	1.25 Re	1.064	0.954	0.953	0.953	0.952	0.943
	1.50 Re	1.035	0.800	0.797	0.797	0.795	0.778
	1.75 Re	1.010	0.612	---------	0.606	0.598	0.576
	2.00 Re	1.011	0.421	---------	0.577	0.371	0.377
BH (DZP)	0.75 Re	1.085	0.914	0.912	0.912	0.913	0.901
	1.00 Re	0.777	0.601	0.599	0.600	0.600	0.594
	1.25 Re	0.354	0.210	0.212	0.212	0.210	0.209
	1.50 Re	-0.091	-0.117	-0.117	-0.117	-0.119	-0.115
	1.75 Re	-0.490	-0.289	-0.341	-0.306	-0.298	-0.285
	2.00 Re	-0.827	-0.302	--------	-0.394	-0.321	-0.300

Table 2.4

Dipole values of three test systems through ECC (n) methods at stretched geometry in bigger basis set calculation in (a. u.).

System (basis)	Geometry	RHF	ECC(4)	ECC(5*)	Cubic-ECC	NCCSD
	0.75 Re	0.592	0.573	0.574	0.574	0.574
	1.00 Re	0.755	0.714	0.716	0.716	0.714
HF	1.25 Re	0.939	0.852	0.856	0.856	0.853
(aug-cc-	1.50 Re	1.138	0.956	0.955	0.957	0.954
pVQZ)	1.75 Re	1.347	0.978	------	0.974	0.972
	2.00 Re	1.560	0.893	------	0.920	0.873
	0.75 Re	0.693	0.671	0.671	0.671	0.671
	1.00 Re	0.777	0.730	0.732	0.732	0.730
H$_2$O	1.25 Re	0.839	0.749	0.752	0.753	0.749
(aug-cc-	1.50 Re	0.873	0.710	0.722	0.717	0.710
pVTZ)	1.75 Re	0.897	0.627	------	0.640	0.623
	2.00 Re	0.923	0.523	-------	0.554	0.494
	0.75 Re	0.974	0.843	0.841	0.841	0.842
	1.00 Re	0.685	0.556	0.555	0.555	0.556
BH	1.25 Re	0.256	0.163	0.163	0.163	0.163
(aug-cc-	1.50 Re	-0.249	-0.226	-0.226	-0.225	-0.226
pVTZ)	1.75 Re	-0.772	-0.498	-0.520	-0.493	-0.501
	2.00 Re	-1.272	-0.587	----------	-0.568	-0.604

2.4.2.2 H$_2$O

It is a well established fact that symmetrical bond stretching of H$_2$O is a difficult problem and can be used as a good test of an approximate method [41, 42]. As the bonds are stretched, the single determinant reference function provides progressively less satisfactory description, which can be quantitatively reflected by large amplitudes in coupled cluster wave function.

It is clear from the Table 2.3 that for H$_2$O molecule similar trend of dipole values are obtained as for that of the HF molecule. ECC (5*) dipole moment values are closer to the full CI values in comparison to ECC (4). Similar to the case of the HF molecule there is no convergence for ECC (5*) equations at 1.75 and 2.0 Re. from 0.75 to 1.5 Re, ECC (4), ECC (5*), Cubic ECC and NCC all provide the similar quality of results and all are within the range of ± 0.002 a.u. with respect to full CI values in DZ basis. At 1.75 and 2.0 Re ECC (4) dipole moment values are 0.04 and 0.05 a.u. higher than the full CI values respectively. It is again interesting to note that at 2.0 Re, although ECC (4) dipole values differ significantly from full CI, its performance is significantly better than cubic-ECC.

In Table 2.4 where same calculation has been performed in aug-cc-pVTZ basis, we observe that ECC (4) values are very close to NCC dipole values up to 1.75 Re. Its performance is better than the cubic ECC at all the stretched geometries beyond 1.0 Re.

2.4.2.3 BH

We observe that for BH molecule in DZP basis ECC (5*) dipole values are slightly better than ECC (4) compared to full CI up to 1.5 Re. At 1.75 Re, ECC (5*) equations converge, but provide significantly poor results in comparison to ECC (4) method. The inferiority of ECC (5*) results over those of ECC (4) is probably due to the absence of the term $(\Sigma_2'^2 V_N \Sigma_2^2)/4$ in ECC (5*) functional, which not only severely causes convergence difficulty, but also accounts for an

imbalance between Σ_2 and Σ_1 determining equations. As we have already discussed, the dipole moment through ECC (4) is correct at least up to second order, while in ECC (5*) the same is correct up to third order, which is an obvious reason for providing better dipole values through ECC (5*) than that of ECC (4). But at the far away from the equilibrium geometry when Σ amplitudes are enormously increased, $V_N^{(1)}\Sigma_2$ term also becomes a leading term along with the $F_N^{(1)}\Sigma_1$ term. Hence a proper and balanced treatment of Σ_2 amplitudes (strictly correct up to 4th order) becomes essential.

In case of BH molecule, results of ECC (4) are probably the most attractive. For the first time in our calculation the ECC (4) values seems to be even more accurate than NCC dipole values up to 2.0 Re in DZP basis. Exactly similar pattern of data has been observed from Table 2.4, where same calculation is performed in aug-cc-pVTZ basis.

2.5 Final thoughts and future directions:

From the above discussions, we found that ECC (4) method with singles and doubles for dipole moment works reasonably well at least up to 1.75 Re, while ECC (5*) method works properly only up to 1.5 Re. The absence of $(\Sigma_2'^2 V_N \Sigma_2^2)/4$ term in ECC (5*) functional is probably the primary reason for severe convergence difficulty as well as for providing poor dipole values beyond 1.5 Re. Both the ECC (4) and ECC (5*) methods are fully variational as well as size extensive and follow the (2n+1) rule. The overall performance of ECC (4) method even with singles and doubles is really attractive. ECC (4) results are significantly better than cubic-ECC especially at 2.0 Re. Dipole moment obtained through ECC (4) is correct only up to second order whereas the same through ECC (5*) is correct up to partially third order. The inclusion of the missing quartic term in ECC (5*) functional might be interesting to analyze numerically and is presently under study. In ECC (4) method excitation and de- excitation amplitude equations are

decoupled from each other and hence it is computationally simpler than ECC (5*) as well as cubic truncated ECC. It is gratifying to note that in spite of absence of several higher order (quadratic, cubic as well as quartic) terms in ECC (4) functional compared to NCCSD, it provides very good quality results for dipole moment, which are close to NCCSD dipole values. This makes us more confident to further proceed with ECC (4) and ECC (5*) schemes for second and third order response properties. At last, it is extremely desirable to test numerically the improvement in the performance of ECC (n) methods for the higher order molecular response properties with the inclusion of partial non iterative as well as full triples.

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Chapter 3

A Lagrange multiplier approach for excited state properties through Intermediate Hamiltonian formulation of Fock space multi-reference coupled-cluster theory

In this chapter, we present a formulation based on Lagrange multiplier approach for efficient evaluation of excited state energy derivatives in Fock space coupled cluster theory within the Intermediate Hamiltonian framework. The formulation is applied to derive the explicit generic expressions up to second order energy derivatives for [1, 1] sector of Fock space with singles and doubles approximation. Its advantage, efficiency and interconnection in comparison to the Lagrange multiplier approach in traditional formulation of Fock space, which is built on the concept of Bloch equation based effective Hamiltonian, has been discussed. Computational strategy for their implementation has also been discussed in some detail.

3.1 Introduction:

In chapter 1, we have briefly discussed the general overview of the electronic structure theory and the linear response approach for atomic and molecular properties. In chapter 2, we presented and implemented in particular a variational variant of single reference coupled cluster (SRCC) method i. e. extended CC (ECC) method for molecular response properties for the ground state of molecular systems. This chapter is mainly focused on the development of an efficient approach for evaluation of excited state molecular response properties using intermediate Hamiltonian formulation of Fock space multi-reference coupled cluster theory (IHFSMRCC).

Single reference coupled cluster (SRCC) method [1-10] is known to be among the most efficient tools for the treatment of electron correlation effects of closed shell molecular systems in cases, where a single determinant provides a good zeroth order description. Among its many advantages, accurate treatment of dynamic electron correlation and size-extensivity are particularly important. These features have made SRCC method widely applicable for the calculation of correlation energy, molecular properties, gradients and potential energy surfaces [6-10]. The success of single reference CC method has motivated many workers to extend the method for quasi degenerate situations with the help of higher excitations [10, 11]. However, in cases of molecular bond dissociation and open shell states, a multi-reference zeroth order description becomes essential for the treatment of non-dynamic electron correlation and dynamic correlation is taken care of by the built in exponential feature of wave operator. These methods are collectively referred to as multi-reference coupled cluster (MRCC) [12-20] methods. Existing MRCC approaches can be divided into three basic categories: Fock space (FS) [12, 13] or valence universal (VU), Hilbert space (HS) [14] or state universal (SU) and state selective (SS) [15-20] CC. The first two approaches are commonly in the class of multi-root MRCC methods, as they are built on the concept of Bloch equation

based effective Hamiltonian [21, 22] acting within a model space. It is important to mention here that several methods based on SRCC have been extensively developed, which are widely applicable in quasi-degenerate situations. [23-30] Within single reference framework, method of moments coupled cluster (MMCC) [23], coupled cluster linear response (CCLR) [24-27], equation of motion coupled cluster (EOMCC) [28-30], symmetry-adapted cluster configuration interaction (SAC-CI) [31], similarity transformed EOMCC (STEOMCC) [32, 33] and spin flip EOMCC (SF-EOMCC) [34] methods are commonly used to handle quasi degeneracy problems. Although these methods structurally differ from MRCC method in many aspects, their high accuracy, relative simplicity and cost effectiveness are important to note.

In this chapter, we focus on FSCC method [35-48]. The FSMRCC method has been successfully used for difference energy calculations. However, in several cases when model space is increased in order to target more excited states, the method faces convergence difficulties. This is termed as intruder state [49, 50] problem. The intermediate Hamiltonian [51] formulation of FSMRCC (IHFSMRCC) [52-61] method provides a more efficient and reliable as well as numerically stable way to handle the intruder state problem. Intruder state problem can also be avoided by using SSMRCC methods. Among few variants of SSMRCC method in literature are Brillouin-Wigner (BW) MRCC [15, 16] ansatz, exponential MR wave function ansatz (MRexpT) [17], the state- specific MRCC method suggested by Mukherjee and coworkers (Mk-MRCC) [18] and internally contracted MRCC (ic-MRCC) [19] theory. Recently, Nooijen and co-workers proposed multi-reference EOMCC (MR-EOMCC) [20] theory.

The idea of intermediate Hamiltonian was first introduced by Malrieu [51] *et al* in the context of degenerate perturbation theory. Various kinds of intermediate Hamiltonian schemes have been developed and implemented by several workers. Meissner has applied the intermediate Hamiltonian technique to reformulate the

FSCC method for excitation energy [52-54]. The eigenvalue-independent-partitioning (EIP) [62] technique by Sinha *et al* can also be treated as a specific implementation of intermediate Hamiltonian in Fock space. The IH formulation of FSMRCC, which leads to a completely new method, has been developed and extensively applied by Kaldor and coworkers [63, 64].

Formulation of efficient theoretical as well computational technique for the evaluation of molecular properties in FSMRCC method is quite desirable in order to increase the scope and applicability of the method. The linear response in effective Hamiltonian based FSMRCC method was initiated by Pal [65] and then implemented by Pal and coworkers for the first order properties [66, 67]. The linear response approach in SRCC method was first formulated by Monkhorst [6(a)] and further developed and applied by Bartlett and coworkers, who introduced the Z-vector [68] technique within the SRCC framework [69]. With the help of Z vector method, the evaluation of cluster amplitude derivatives for each mode of perturbation can be eliminated with the cost of solving a linear equation, which is independent of external perturbation. Jorgensen and coworkers [70] formulated Lagrange multiplier approach (LMA), based on Lagrange method of undetermined multipliers in SRCC framework. The final equations are shown to be equivalent to those obtained through Z vector technique, but this approach is found to be suitable for higher order derivatives. The LMA approach has been extensively used by various groups for energy derivative formulation. Stanton and Gauss implemented analytic gradients within EOMCC framework [71]. Nooijen and coworkers used LMA approach in STEOMCC formulation for the calculation of gradients [33]. Recently, Krylov *et al* implemented analytic gradients using SF-EOMCC method [72]. Gauss and co-workers have formulated and implemented analytic gradients for Mk-MRCC method [73]. Pittner et al implemented analytic gradients for the SU and BW-MRCC approaches [74]. Ajitha and Pal developed the Z-vector like formalism in FSMRCC [75, 76] framework, which eliminated

the highest sector cluster response quantities. The extension of Lagrange multiplier approach in FSMRCC theory using complete model space for the first order energy derivatives was initiated by Szalay [77]. This approach was further generalized for general incomplete model space by Shamasundar et al. [78, 79] for higher order energy derivatives and also implemented by Pal and coworkers [80-83].

As mentioned earlier, the traditional effective Hamiltonian based FSMRCC theory suffers from intruder states. The intermediate Hamiltonian formulation of Meissner [52] provides an alternative way to reach the convergence in a more efficient manner with larger model space. This not only helps one to obtain more number of states, but also, in several cases, significantly improves the correlation effects. Apart from these advantages, a considerable amount of computational simplicity arises due to two reasons. The first one is that unlike the case of effective Hamiltonian based FSMRCC, the equations for cluster amplitudes are not solved in a coupled iterative manner. The second reason is the decoupling of the highest sector cluster amplitudes from the eigenvalue problem. A similar analogy can be expected for the excited state energy derivatives also. Hence, in our opinion, it is desirable to extend the LMA [70, 77, 78] in IHFSMRCC formulation of Meissner for energy derivatives, in order to obtain excited state properties for desired number of states with bigger basis sets and larger model space in numerically stable and cost effective way. The same is the objective of this chapter.

The chapter is organized as follows. In section 3.2, we discuss the general concept of FSMRCC based on effective Hamiltonian theory. In section 3.3, IHFSMRCC formulation of Meissner has been discussed. In section 3.4, LMA has been applied in IHFSMRCC framework to derive expressions up to 2nd order energy derivatives. Section 3.5 is dedicated to the discussion regarding the computational strategy for solving the equations as well as the advantages of the present

formulation over the traditional one. Finally, section 3.6 contains a brief discussion of major conclusions and future directions of the work.

3.2 Effective Hamiltonian formulation of FSMRCC theory:

The FSMRCC theory [35-48] is originally based on the concept of effective Hamiltonian (EH) [12, 13]. This uses a common vacuum with respect to which holes and particles are defined. These holes and particles are further classified as active and inactive ones. The model space is then constructed by a linear combination of suitably chosen (based on energetic criteria) active configurations. The contribution from the orthogonal complement of the model space is included through wave operator, which is used to construct the effective Hamiltonian. This effective Hamiltonian is diagonalized to get the contribution from the model space configurations. Although in the case of incomplete model space the equations are modified but the basic qualitative idea remains same.

The principle idea of effective Hamiltonian theory is to extract some of the eigenvalues of Hamiltonian from the whole eigenvalue spectrum. To obtain this, the configuration space is divided into model and orthogonal space, denoted as M and $M_\perp$ respectively. Let us denote the projection operator of these two mutually orthogonal spaces as P_M and Q_M respectively. The model space is chosen in such a manner that its linear combination can provide a good zeroth order description of the eigenstates, in which we are interested. In practice, molecular orbital (MO) picture is being used to define the model space by choosing the close lying valence occupied and virtual orbitals. A given number of electrons are distributed among these orbital's to generate the model space configurations. If the model space contains all the configurations, generated by distributing the valence electrons among the entire valence orbital's in all possible ways, it is termed as complete model space (CMS), and otherwise it is an incomplete model space (IMS). Let us consider the Schrodinger equation for desired (say m[th]) eigenstates,

$$H_N \Psi_m = \Delta E_m \Psi_m \qquad (3.1)$$

We have used the normal ordered form of the Hamiltonian, $H_N = H - E_{HF}$ and $\Delta E_m = E_m - E_{HF}$.

Normal ordered Hamiltonian, in second quantization, is

$$H_N = \sum_{p,q} f_{pq} . \{p^+ q\} + \frac{1}{4} \sum_{p,q,r,s} W_{pqrs} \{p^+ r q^+ s\} \qquad (3.2)$$

The f_{pq} refer to appropriate parts of the Fock operator. The W_{pqrs} are antisymmetrized two electron integrals. The projection operator P_M of the model space acts on the exact eigenstates to generate the model function Ψ_m^o which is defined within the model space.

$$P_M \Psi_m = \Psi_m^o \qquad (3.3)$$

Defining a wave operator Ω, which acts only on the model space (i.e., $\Omega = \Omega P_M$) and transforms the model function into the exact eigenstates,

$$\Psi_m = \Omega \Psi_m^o \qquad (3.4)$$

We further define an operator $H_{N,eff}$ in such a way that,

$$H_{N,eff} \Psi_m^o = \Delta E_m \Psi_m^o \qquad (3.5)$$

By using the definition of Ω, P_M and with the help of Eq. (3.1), we obtain the well known generalized Bloch-Lindgren equation [8] in normal ordered form as,

$$H_N \Omega P_M = \Omega H_{N,eff} P_M \qquad (3.6)$$

The Bloch projection approach to solve the above equation involves left projection of P_M and Q_M leading to,

$$Q_M (H_N \Omega - \Omega H_{N,eff}) P_M = 0 \tag{3.7}$$

$$P_M (H_N \Omega - \Omega H_{N,eff}) P_M = 0 \tag{3.8}$$

To solve the above equations an additional normalization condition is imposed to fix $P_M \Omega P_M$ by parameterization of Ω. Usually this is employed by imposing the intermediate normalization condition $P_M \Omega P_M = P_M$ especially to the CMS. In general, the set of equations for Ω and $H_{N,eff}$ are coupled to each other through Eqs. (3.7) and (3.8) and in general $H_{N,eff}$ cannot be expressed explicitly in terms of Ω. However, when intermediate normalization is imposed, $H_{N,eff}$ can directly be written as a function of Ω. In this case Eq. (3.8) can be written as,

$$P_M H_N \Omega P_M = P_M H_{N,eff} P_M \tag{3.9}$$

After solving the equations for Ω and $H_{N,eff}$, diagonalization of $H_{N,eff}$ within the model space provides the desired eigenvalues as,

$$H_{N,eff} C = CE \tag{3.10}$$

$$\tilde{C} H_{N,eff} = E\tilde{C} \tag{3.11}$$

$$\tilde{C} C = C\tilde{C} = 1 \tag{3.12}$$

Where, C ($\tilde{C}$) is the square matrix of dimension P_M, containing the columns (rows) of right (left) eigenvectors of $H_{N,eff}$ and E is the diagonal eigenvalue matrix.

In the Fock space or valence universal MRCC approach Ω is defined as,

$$\Omega = \{e^{\tilde{S}^{(k,l)}}\} P_M \tag{3.13}$$

Where, { } denotes the normal product form of expansion as defined by Lindgren.[37] In this formulation Ω is valence universal which means that same Ω solves all the sectors. Its cluster structure can be written as,

$$\tilde{S}^{(i,j)} = \sum_{i=0}^{i=m} \sum_{j=0}^{j=n} S^{(i,j)} \tag{3.14}$$

Where, $S^{(i,j)}$ is the cluster operator and normal ordering is defined with respect to vacuum Φ. The maximum number of valence particles and holes in Φ are denoted by m and n, respectively. The cluster operators $S^{(i,j)}$ induces hole-particle excitations out of each of model spaces $P^{(i,j)}$ containing i valence particle and j valence hole with respect to Φ. The cluster operators $S^{(i,j)}$ contain i valence particle and j valence hole destruction operator. Contraction between different cluster operators is avoided due to normal ordering leading to partial hierarchical decoupling referred to as sub system embedding condition (SEC) [35].

For simplicity, here onwards, we will denote the cluster operator of (0, 0) sector, $S^{(0,0)}$ as $T^{(0,0)}$ or sometimes simply as T. The final working equation for FSMRCC for CMS (and some of the special IMS) can be written as,

$$Q_M (\overline{H}_N \{e^S\} - \{e^S\} H_{N,eff}) P_M = 0 \tag{3.15}$$

$$H_{N,eff} = P_M \overline{H}_N \{e^S\} P_M \tag{3.16}$$

3.3 Intermediate Hamiltonian formulation of FSMRCC theory:

In this chapter we have followed the terminology used by Meissner [52] to define the intermediate Hamiltonian formulation of FSMRCC theory. As mentioned earlier, $H_{N,eff}$ is defined in the space (model space) with dimension (say, m) much smaller than the actual Hamiltonian, its diagonalization provides desired eigenvalues. When model space configurations (P_M) are not energetically well

separated from those of complementary space (Q_M), the method faces convergence problem, termed as intruder state problem. The basic idea of IH formulation is to divide the configuration space into three subspaces namely main, intermediate and outer space (see figure 1) with the projection operators P_M, P_I and Q_o respectively [51]. The intermediate space is imposed as a buffer between main and outer space. This intermediate space can be defined formally in terms of excitation level of highest sector cluster operators which defines the FSMRCC equations. The main space of IH formulation is same as the model space of effective Hamiltonian theory, while the intermediate space (P_I) has been obtained from the complementary space (Q_M) of EH theory by further dividing it into two parts: the intermediate and the outer space.
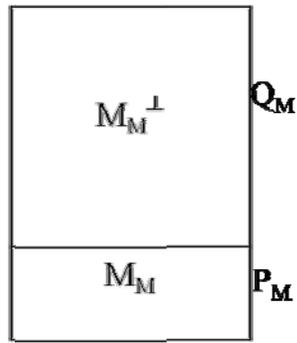
Fig 1a: Effective Hamiltonian Approach   b: Intermediate Hamiltonian Approach
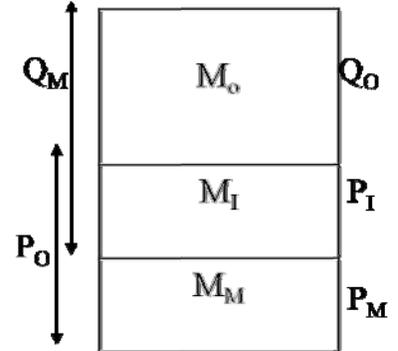
Diagonalization of intermediate Hamiltonian provides the eigenvalues from which only a subset of roots, corresponding to main space, are equivalent to those obtained through effective Hamiltonian theory. In this formulation the final working eq. of FSMRCC can be rewritten as,

$$P_I(\overline{H}_N\{e^S\}-\{e^S\}H_{N,eff})P_M = 0 \tag{3.17}$$

$$H_{N,eff} = P_M \overline{\overline{H}}_N\{e^S\}P_M \tag{3.18}$$

Defining the operators X as,

78

$$X = \{e^S - 1\}P_M \tag{3.19}$$

X is defined in such a way that it satisfies,

$$X = Q_M X P_M, \quad X^2 = 0 \tag{3.20}$$

Eqs. (3.17) and (3.18) can be written in terms of X as,

$$P_I(1-X)\overline{H}_N(1+X)P_M = 0 \tag{3.21}$$

$$P_M(1-X)\overline{H}_N(1+X)P_M = H_{N,eff} \tag{3.22}$$

Eqs. (3.21) and (3.22) describe a two step procedure. The first is to solve the quadratic Eq. of X and the second one is to diagonalize $H_{N,eff}$ to obtain the m number of roots, where m is the dimension of the main space. If Eq. (3.21) is satisfied, the same m number of eigenvalues can be obtained by diagonalization of the operator $(1-X)\overline{H}_N(1+X)$ within the $P_o = P_M + P_I$ space. We can replace this two step method with a single step of matrix diagonalization in the following manner. Let us divide the operator X into Y and Z as,

$$X=Y+Z \tag{3.23}$$

$$Y = Q_O X P_M, \quad Z = P_I X P_M \tag{3.24}$$

And $Q_M = P_I + Q_O$ \hfill (3.25)

Using the properties of Y and Z, the operator $(1-X)\overline{H}_N(1+X)$ can be written as,

$$(1-X)\overline{H}_N(1+X) = (1-Z)(1-Y)\overline{H}_N(1+Y)(1+Z) \tag{3.26}$$

It is clear from the definition of X (also for Y and Z),

$$(1-X) = (1+X)^{-1} \tag{3.27}$$

From the above interpretation it is clear that if Eq. (3.21) is satisfied, the m number of roots can be extracted equivalently via diagonalization of $(1-X)\overline{H}_N(1+X)$ or $(1-Y)\overline{H}_N(1+Y)$ operator within $P_O - P_O$ space, as both the operators are related to each other through similarity transformation with respect to an operator $(1+Z)$. Finally we define the Intermediate Hamiltonian as,

$$H_I = P_O(1-Y)\overline{H}_N(1+Y)P_O \tag{3.28}$$

Using the fact that P_M, P_I and Q_o are the projection operators of the mutually orthogonal space,

Eq. (3.28) can be finally written as,

$$H_I = P_O\overline{H}_N(1+Y)P_O = P_O\overline{H}_N P_O + P_O\overline{H}_N Y P_M \tag{3.29}$$

For solving the above Eq. we assume that the equations for (0, 0) sector, which is essentially the same as standard SRCC equation, has already been solved. For (0, 1) and (1, 0) sectors,

$$Y^{(0,1)} = Y^{(1,0)} = 0 \tag{3.30}$$

$$X^{(0,1)} = Z^{(0,1)} = S^{(0,1)} \tag{3.31}$$

$$X^{(1,0)} = Z^{(1,0)} = S^{(1,0)} \tag{3.32}$$

For (0, 1) sector (similarly for (1, 0) sector also), the Intermediate Hamiltonian can be written as,

$$H_I^{(0,1)} = P_O^{(0,1)}\overline{H}_N P_O^{(0,1)} \tag{3.33}$$

Hence for solving the eigenvalue problem for (0, 1) and (1, 0) sectors, $\overline{H}_N$ has to be diagonalized within the space spanned by 1h, 2h1p (one hole and two holes and one particle) and 1p, 2p1h (one particle and two particles and one hole) determinants respectively. Hence it is very transparent to see in IHFSCC

framework that eigenvalues of one valence sectors are independent of the choice of model space and the method becomes identical to the IP/EA-EOMCCSD [84, 85] method. However, for solving the (1, 1) sector (or alternatively (0, 2) and (2, 0) sectors also), cluster amplitudes for (0, 1) and (1, 0) sectors are required explicitly, and it becomes essential to define the model space by choosing some of the valence holes/particles as active. The cluster amplitudes for one-valence sectors can be obtained by imposing the intermediate normalization condition on the set of selectively chosen eigenvectors corresponding to the active holes/particles. The matrix formed through column wise arrangement of these eigenvectors can be divided into two sub-matrices. The first one is V_O, obtained from the model space coefficients and the second one is V, obtained from the rest of the matrix. Hence the cluster amplitudes for (0, 1) sector (similarly for (1, 0) sector also) can be obtained as [52, 62]

$$Z^{(0,1)} = [VV_O^{-1}]^{(0,1)} = P_I^{(0,1)} S^{(0,1)} P_M^{(0,1)} \tag{3.34}$$

Intermediate Hamiltonian matrix for (1, 1) sector is given by,

$$H_I^{(1,1)} = P_O^{(1,1)} \overline{H_N} P_O^{(1,1)} + P_O^{(1,1)} \overline{H_N} Y^{(1,1)} P_M^{(1,1)} \tag{3.35}$$

Where X, Y and Z operators for (1, 1) sectors are defined as,

$$X^{(1,1)} = Y^{(1,1)} + Z^{(1,1)} \tag{3.36}$$

$$Y^{(1,1)} = Q_O^{(1,1)} \{ S_2^{(0,1)} + S_2^{(1,0)} + S_1^{(0,1)} S_2^{(1,0)} + S_1^{(1,0)} S_2^{(0,1)} + S_2^{(0,1)} S_2^{(1,0)} \} P_M^{(1,1)} \tag{3.37}$$

$$Z^{(1,1)} = P_I^{(1,1)} \{ S_1^{(0,1)} + S_1^{(1,0)} + S_1^{(0,1)} S_1^{(1,0)} + S_2^{(1,1)} \} P_M^{(1,1)} \tag{3.38}$$

It is clear from the Eq. (3.35) that intermediate Hamiltonian for (1, 1) sector can be constructed by the matrix representation of $\overline{H_N}$ within the 1h1p (one hole and one particle determinants) space, modified by the term containing $Y^{(1,1)}$. As $Y^{(1,1)}$ does not contain the $S^{(1,1)}$ amplitudes, the IH matrix for (1, 1) sector can be constructed

from the knowledge of cluster amplitudes of lower sectors. Hence, we can conclude that the cluster determining equation for the highest sector (1, 1) is decoupled from the eigenvalue problem within IH framework. However the $S^{(1,1)}$ amplitudes can also be determined, if precisely required. Analogous to the case of one valence sectors, this again can be obtained by imposing the intermediate normalization condition on the selectively chosen eigenvectors as,

$$Z^{(1,1)} = [VV_O^{-1}]^{(1,1)} \tag{3.39}$$

It is important here to mention that both connected as well disconnected diagrams appears in Eq. (3.35), as there is no explicit cancellation of disconnected terms. However, this cancellation occurs implicitly during the process of diagonalization. Hence linked cluster theorem holds in this manner. As long as the original (effective Hamiltonian based) FSMRCC Eqs. is given by Eqs. (3.15) and (3.16), its reformulation through intermediate Hamiltonian technique (given by Eq. 3.28), is straightforward. This is usually the case of CMS and some of the special IMS (like (1, 1) sector), where $H_{N,eff}$ is explicitly expressible in terms of Ω. This strategy has been used very recently by Musial et al to extend the IH formulation and its implementation for (0, 2) and (2, 0) sectors   [61, 62].   In this IH formulation of FSMRCC theory, equations don't have to be solved in coupled iterative manner. Rather, the eigenvalues are obtained through direct diagonalization procedure. This helps one to safely reach the convergence with larger model space, which significantly improves the correlation effects in many cases. Also as the final diagonalization occurs in 1h1p space, this allows one to perform the calculation with significantly larger basis set.

An obvious next step in the context of IHFSMRCC theory is to extend the formulation for excited state properties also, in order to extend the applicability of the method. In the next section we present a formulation based on Lagrange multiplier approach for energy derivatives for FSMRCC theory in IH framework.

3.4. Lagrange multiplier approach for IH formulation of FSMRCC:

The energy derivatives can be most easily obtained by using the Lagrange multiplier approach [56], which is based on Lagrange method of undetermined multipliers. In this method we define a functional ($\Im$, a scalar quantity), which consist a explicit energy expression along with equations that define all the quantities appearing in the energy expression, each multiplied by an undetermined parameter. After making the functional stationary with respect to Lagrangian multipliers, cluster amplitudes determining equations are obtained, which are already satisfied due to energy equations. Making the functional stationary with respect to cluster amplitudes, leads to the linear equations which determine the Lagrangian multipliers. The Lagrangian functional is defined for a specific eigenstate. When the stationary conditions are satisfied, the energy derivatives with respect to external perturbation can be directly obtained in terms of Hamiltonian matrix derivatives along with the cluster amplitudes and Lagrange multipliers. In this way the evaluation of cluster amplitude derivatives for each mode of perturbation can be eliminated at the expense of solving a linear equation in Lagrange multiplier, which are independent of external perturbation. This hierarchy can be extended for the higher order energy derivatives which leads to (2n+1) and (2n+2) rules for cluster amplitudes and Lagrange multipliers respectively. This means that (2n+1)th and (2n+2)th order energy derivatives can be obtained only with the knowledge of up to nth order derivatives of cluster amplitudes and Lagrangian multipliers respectively.

Unlike effective Hamiltonian based FSMRCC, in the IHFSCC framework the highest sector cluster amplitudes are decoupled from the eigenvalue problem. Apart from handling the intruder states problem, this decoupling can be further exploited for the efficient evaluation of energy derivatives using the Lagrange multiplier approach. In this section we derive the explicit generic expressions for the 1st and 2nd order energy derivatives of (1, 1) sector of Fock space within IH

framework, using the Lagrange multiplier approach. As mentioned earlier, IH formulation of FSCC method for (0, 1) and (1, 0) sectors is identical to the IP/EA-EOMCC [84, 85], its energy derivative formulation also turns out to be identical with the LMA-IP/EA-EOMCC. This LMA-IP-EOMCC has already been implemented by Stanton for gradients [86]. Although in this section we derive our expressions for specific case of (1, 1) sectors, the basic structure of equations and the final form of the expression remains same for any sector with CMS.

We define Lagrangian functional for (1, 1) sector in IH formulation of FSMRCC theory as,

$$\Im = \langle 0 | L^{(1,1)} H_{Int}^{(1,1)} R^{(1,1)} | 0 \rangle + P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} (1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)}) P_M^{(0,1)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} (1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)}) P_M^{(1,0)}$$

$$+ P_M^{(0,0)} \Lambda^{(0,0)} P_I^{(0,0)} \bar{H}_N P_M^{(0,0)} - E_\mu [\langle 0 | L^{(1,1)} R^{(1,1)} | 0 \rangle - 1] \qquad (3.40)$$

Where $L^{(1,1)}$ and $R^{(1,1)}$ denote the left and right eigenvectors of intermediate Hamiltonian matrix respectively. After making the above functional stationary with respect to all the parameters, we find,

$$\frac{\partial \Im}{\partial \Lambda^{(0,0)}} = 0 \Rightarrow P_I^{(0,0)} \bar{H}_N P_M^{(0,0)} = 0 \qquad (3.41)$$

$$\frac{\partial \Im}{\partial \Lambda^{(0,1)}} = 0 \Rightarrow P_I^{(0,1)} (1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)}) P_M^{(0,1)} = 0 \qquad (3.42)$$

$$\frac{\partial \Im}{\partial \Lambda^{(1,0)}} = 0 \Rightarrow P_I^{(1,0)} (1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)}) P_M^{(1,0)} = 0 \qquad (3.43)$$

$$\frac{\partial \Im}{\partial L^{(1,1)}} = 0 \Rightarrow H_{Int}^{(1,1)} R^{(1,1)} | 0 \rangle = E_\mu R^{(1,1)} | 0 \rangle \qquad (3.44)$$

$$\frac{\partial \Im}{\partial R^{(1,1)}} = 0 \Rightarrow \langle 0 | L^{(1,1)} H_{Int}^{(1,1)} = E_\mu \langle 0 | L^{(1,1)} \qquad (3.45)$$

$$\frac{\partial \Im}{\partial E_\mu} = 0 \Rightarrow \langle 0 | L^{(1,1)} R^{(1,1)} | 0 \rangle = 1 \tag{3.46}$$

$$\frac{\partial \Im}{\partial S^{(0,1)}} = 0 \Rightarrow P_M^{(0,1)} L^{(1,1)} [H_{Int}^{(1,1)}]_{S^{(0,1)}}^{(1)} R^{(1,1)} P_I^{(0,1)}$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]_{S^{(0,1)}}^{(1)} P_I^{(0,1)} = 0 \tag{3.47}$$

$$\frac{\partial \Im}{\partial S^{(1,0)}} = 0 \Rightarrow P_M^{(1,0)} L^{(1,1)} [H_{Int}^{(1,1)}]_{S^{(1,0)}}^{(1)} R^{(1,1)} P_I^{(1,0)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]_{S^{(1,0)}}^{(1)} P_I^{(1,0)} = 0 \tag{3.48}$$

$$\frac{\partial \Im}{\partial T^{(0,0)}} = 0 \Rightarrow P_M^{(0,0)} L^{(1,1)} [H_{Int}^{(1,1)}]_{T^{(0,0)}}^{(1)} R^{(1,1)} P_I^{(0,0)}$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]_{T^{(0,0)}}^{(1)} P_I^{(0,0)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]_{T^{(0,0)}}^{(1)} P_I^{(0,0)}$$

$$+ P_M^{(0,0)} [\bar{H}_N]_{T^{(0,0)}}^{(1)} P_I^{(0,0)} = 0 \tag{3.49}$$

In the above equations, subscripts $S^{(0, 1)}$, $S^{(1, 0)}$ and $T^{(0, 0)}$ indicate differentiation of expression in square brackets with respect to cluster operator of corresponding sectors, while superscript represents the order of differentiation. In case of differentiation with respect to external perturbation, no subscript will be used. From here onwards, we will follow the same notation throughout our derivation.

Optimizing the functional with respect to all the parameters, we obtain the FSMRCC amplitude equations, eigenvalue equations for target state with bi-orthonormality condition and the equations for determining lambda amplitudes of various sectors. The equations have to be solved exactly in the same order they are given above. Due to (SEC), cluster amplitudes of lower sectors are decoupled from the higher sectors and should be solved starting with (0, 0) sector, going upwards up to the (0, 1) and (1, 0) sector. However, this decoupling holds in exactly reverse manner78 for the lambda amplitudes which means that lambda

amplitudes for (0, 1) and (1, 0) sectors are used to determine the lambda amplitudes for (0, 0) sectors. It is important to notice that we are not actually using Eq. (3.42) and (3.43) to get cluster amplitudes for (0, 1) and (1, 0) sectors, rather these are determined through imposing the intermediate normalization condition on IP/EA-EOMCC eigenvectors. However these equations are sufficient to define the cluster amplitudes in equivalent way and hence can be used as constraints. A very similar kind of strategy has been used by Nooijen and coworkers to formulate the gradients of STEOMCC, which is very close to FSMRCC in many respects [32, 33].

Let E_μ be the eigenvalue of a particular (say μth) eigenstate of interest. The nth order energy derivative $E_\mu^{(n)}$, is just the value of functional $\Im^{(n)}$, denoted by $\Im_{opt}^{(n)}$, when the stationary values of all the parameters (denoted as $\{\theta^{(m)}, 0 \leq m \leq n\}$) appearing in the $\Im^{(n)}$, are substituted in it. It is a well established fact that cluster amplitudes and eigenvectors follow the (2n+1) rule and lambda amplitudes and E_μ follow the (2n+2) rule. The quantities which are required to be eliminated with the help of (2n+1) and (2n+2) rule for the first and second order energy derivatives are given below.

$$\Im_{opt}^{(1)} \Rightarrow \{R^{(1)}, S^{(1)}, \Lambda^{(1)}, E_\mu^{(1)}\}$$

$$\Im_{opt}^{(2)} \Rightarrow \{R^{(2)}, S^{(2)}, \Lambda^{(2)}, \Lambda^{(1)}, E_\mu^{(2)}, E_\mu^{(1)}\}$$

Where R represents (both left and right) eigenvectors of desired state and S and Λ denotes the cluster and lambda operators respectively for all the sectors except the (1, 1) sector. The final expression (see appendix A for details) for 1st order energy derivative is given by

$$\mathfrak{I}_{opt}^{(1)} = \left\langle 0 \left| L^{(1,1)} [H_{Int}^{(1,1)}]_{H_N \to H_N^{(1)}}^{(1)} R^{(1,1)} \right| 0 \right\rangle$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]_{H_N \to H_N^{(1)}}^{(1)} P_M^{(0,1)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]_{H_N \to H_N^{(1)}}^{(1)} P_M^{(1,0)} \qquad (3.50)$$

$$+ P_M^{(0,0)} \Lambda^{(0,0)} P_I^{(0,0)} [\bar{H}_N]_{H_N \to H_N^{(1)}}^{(1)} P_M^{(0,0)}$$

The subscript $H_N \to H_N^{(1)}$ refers to the replacement of zeroth-order Hamiltonian H_N by field perturbation operator $H_N^{(1)}$ in expressions in square bracket.

For the evaluation of higher order response properties, 1st order quantities $\theta^{(1)}$ are required in addition. This can be obtained by imposing the condition of stationarity on $\mathfrak{I}^{(1)}$.

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial L^{(1,1)}} = 0 \Rightarrow [H_{Int}^{(1,1)} R^{(1,1)^{(1)}} + H_{Int}^{(1,1)^{(1)}} R^{(1,1)} - E_\mu^{(1)} R^{(1,1)} - E_\mu R^{(1,1)^{(1)}}] \left| 0 \right\rangle = 0 \qquad (3.51)$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial R^{(1,1)}} = 0 \Rightarrow \left\langle 0 \left| [L^{(1,1)^{(1)}} H_{Int}^{(1,1)} + L^{(1,1)} H_{Int}^{(1,1)^{(1)}} - E_\mu^{(1)} L^{(1,1)} - E_\mu L^{(1,1)^{(1)}}] = 0 \right.\right.$$

$$\qquad (3.52)$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial E_\mu} = 0 \Rightarrow \left\langle 0 \left| [L^{(1,1)^{(1)}} R^{(1,1)} + L^{(1,1)} R^{(1,1)^{(1)}}] \right| 0 \right\rangle = 0$$

$$\qquad (3.53)$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial \Lambda^{(0,1)}} = 0 \Rightarrow P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]^{(1)} P_M^{(0,1)} = 0$$

$$\qquad (3.54)$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial \Lambda^{(1,0)}} = 0 \Rightarrow P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]^{(1)} P_M^{(1,0)} = 0$$

$$\qquad (3.55)$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial \Lambda^{(0,0)}} = 0 \Rightarrow P_I^{(0,0)} [\bar{H}_N]^{(1)} P_M^{(0,0)} = 0$$

$$\qquad (3.56)$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial S^{(0,1)}} = 0 \Rightarrow P_M^{(0,1)}\{L^{(1,1)^{(1)}}[H_{Int}^{(1,1)}]_{S^{(0,1)}}^{(1)} R^{(1,1)}$$

$$+ L^{(1,1)}[H_{Int}^{(1,1)^{(1)}}]_{S^{(0,1)}}^{(1)} R^{(1,1)} + L^{(1,1)}[H_{Int}^{(1,1)}]_{S^{(0,1)}}^{(1)} R^{(1,1)^{(1)}}\}P_I^{(0,1)}$$

$$+ P_M^{(0,1)}\Lambda^{(0,1)^{(1)}}P_I^{(0,1)}[(1-X^{(0,1)})\bar{H}_N(1+X^{(0,1)})]_{S^{(0,1)}}^{(1)} P_I^{(0,1)}$$

$$+ P_M^{(0,1)}\Lambda^{(0,1)}P_I^{(0,1)}[(1-X^{(0,1)})\bar{H}_N(1+X^{(0,1)})]_{S^{(0,1)}}^{(1)} P_I^{(0,1)} = 0 \tag{3.57}$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial S^{(1,0)}} = 0 \Rightarrow P_M^{(1,0)}\{L^{(1,1)^{(1)}}[H_{Int}^{(1,1)}]_{S^{(1,0)}}^{(1)} R^{(1,1)}$$

$$+ L^{(1,1)}[H_{Int}^{(1,1)^{(1)}}]_{S^{(1,0)}}^{(1)} R^{(1,1)} + L^{(1,1)}[H_{Int}^{(1,1)}]_{S^{(1,0)}}^{(1)} R^{(1,1)^{(1)}}\}P_I^{(1,0)}$$

$$+ P_M^{(1,0)}\Lambda^{(1,0)^{(1)}}P_I^{(1,0)}[(1-X^{(1,0)})\bar{H}_N(1+X^{(1,0)})]_{S^{(1,0)}}^{(1)} P_I^{(1,0)}$$

$$+ P_M^{(1,0)}\Lambda^{(1,0)}P_I^{(1,0)}[(1-X^{(1,0)})\bar{H}_N(1+X^{(1,0)})]_{S^{(1,0)}}^{(1)} P_I^{(1,0)} = 0 \tag{3.58}$$

$$\frac{\partial \mathfrak{I}^{(1)}}{\partial T^{(0,0)}} = 0 \Rightarrow P_M^{(0,0)}\{L^{(1,1)^{(1)}}[H_{Int}^{(1,1)}]_{T^{(0,0)}}^{(1)} R^{(1,1)}$$

$$+ L^{(1,1)}[H_{Int}^{(1,1)^{(1)}}]_{T^{(0,0)}}^{(1)} R^{(1,1)} + L^{(1,1)}[H_{Int}^{(1,1)}]_{T^{(0,0)}}^{(1)} R^{(1,1)^{(1)}}\}P_I^{(0,0)}$$

$$+ P_M^{(0,1)}\Lambda^{(0,1)^{(1)}}P_I^{(0,1)}[(1-X^{(0,1)})\bar{H}_N(1+X^{(0,1)})]_{T^{(0,0)}}^{(1)} P_I^{(0,0)}$$

$$+ P_M^{(0,1)}\Lambda^{(0,1)}P_I^{(0,1)}[(1-X^{(0,1)})\bar{H}_N(1+X^{(0,1)})]_{T^{(0,0)}}^{(1)} P_I^{(0,0)}$$

$$+ P_M^{(1,0)}\Lambda^{(1,0)^{(1)}}P_I^{(1,0)}[(1-X^{(1,0)})\bar{H}_N(1+X^{(1,0)})]_{T^{(0,0)}}^{(1)} P_I^{(0,0)}$$

$$+ P_M^{(1,0)}\Lambda^{(1,0)}P_I^{(1,0)}[(1-X^{(1,0)})\bar{H}_N(1+X^{(1,0)})]_{T^{(0,0)}}^{(1)} P_I^{(0,0)}$$

$$+ P_M^{(0,0)}\Lambda^{(0,0)}P_I^{(0,0)}[\bar{H}_N]_{T^{(0,0)}}^{(1)} P_I^{(0,0)} = 0 \tag{3.59}$$

The second order energy derivative, $E_\mu^{(2)}$, is same as the value of the functional $\mathfrak{I}^{(2)}$, denoted by $\mathfrak{I}_{opt}^{(2)}$, when the stationary values of $\{\theta^{(n)}, n = 0, 2\}$ are substituted in the functional. The final simplified expression (see appendix B for detail) for second order energy derivative can be written as,

$$\mathfrak{I}_{opt}^{(2)} = \langle 0|L^{(1,1)}\{H_{Int}^{(1,1)}\}_{(T^{(1)},S^{(0,1)^{(1)}},S^{(1,0)^{(1)}})}^{(2)} R^{(1,1)}|0\rangle + P_M^{(0,0)}\Lambda^{(0,0)}P_I^{(0,0)}\{\bar{H}_N\}_{T^{(1)}}^{(2)} P_M^{(0,0)}$$

$$+ P_M^{(0,1)}\Lambda^{(0,1)}P_I^{(0,1)}\{(1-X^{(0,1)})\bar{H}_N(1+X^{(0,1)})\}_{(T^{(1)},S^{(0,1)^{(1)}})}^{(2)} P_M^{(0,1)}$$

$$+ P_M^{(1,0)}\Lambda^{(1,0)}P_I^{(1,0)}\{(1-X^{(1,0)})\bar{H}_N(1+X^{(1,0)})\}_{(T^{(1)},S^{(1,0)^{(1)}})}^{(2)} P_M^{(1,0)}$$

$$- 2[\langle 0|L^{(1,1)^{(1)}} H_{Int}^{(1,1)} R^{(1,1)^{(1)}}|0\rangle - E_\mu \langle 0|L^{(1,1)^{(1)}} R^{(1,1)^{(1)}}|0\rangle] \tag{3.60}$$

The above expression means that the terms containing the response quantities, written as subscript along with their zeroth order cluster operators, have only been retained in the curly bracketed expressions.

3.5 Computational strategy and interconnections between effective and intermediate Hamiltonian energy derivatives:

The computational procedure for getting excited state energy derivatives involves the following steps. The first step is to solve the ground state CCSD equations and obtain T amplitudes after solving SCF. For the efficient computational implementation, one and two body parts of $\bar{H}_N$ are constructed with the help of T and stored in the disk while three body part of $\bar{H}_N$ is being constructed instantly, whenever required. These $\bar{H}_N$ intermediates are used to solve the IH matrix eigenvalue problem for (0, 1) and (1, 0) sectors. As the dimension of IH matrix for (0, 1) and (1, 0) sectors is very large, an efficient diagonalization routine has to be used for solving the eigenvalue problems for few of the selected roots. In practice this is followed by Nakatsuji-Hirao algorithm [87] of non symmetric matrices, which is the generalization of Davidson algorithm [88] for symmetric matrices. Once the eigenvalue problem is solved, eigenvectors for selective roots are transformed into the $S^{(0,1)}$ and $S^{(1,0)}$. These S amplitudes are used to construct the IH matrix for (1, 1) sector and solve the eigenvalue problem. The next step is to solve for Λ amplitudes of (0, 1), (1, 0) and (0, 0) sectors through equations defined earlier. As stated earlier, the zeroth order Λ amplitudes itself are sufficient in order to evaluate the 1st as well as 2nd order derivatives while 1st order cluster response are required in addition to obtain the 2nd order energy derivative. The cluster amplitude derivative for (0, 0) sector is obtained through standard procedure of linear response which is given by Eq. (3.56). With the help of T and $T^{(1)}$, IH derivative matrix for (0, 1) and (1, 0) can be constructed. It is important to notice that cluster response for (0, 1) and (1, 0) sectors can be obtained with the

help of selective eigenvectors derivative which is the consequence of the fact that cluster amplitudes of these sectors can be directly obtained through set of chosen eigenvectors. These eigenvector derivatives can be obtained through differentiating the eigenvalue equations as follows.

$$H_{Int}^{(0,1)} R_\mu^{(0,1)} |0\rangle = E_\mu^{(0,1)} R_\mu^{(0,1)} |0\rangle \tag{3.61}$$

$$\langle 0 | \bar{R}_\mu^{(0,1)} R_\mu^{(0,1)} |0\rangle = 1 \tag{3.62}$$

$$\{ H_{Int}^{(0,1)^{(1)}} R_\mu^{(0,1)} + H_{Int}^{(0,1)} R_\mu^{(0,1)^{(1)}} \} |0\rangle = \{ E_\mu^{(0,1)^{(1)}} R_\mu^{(0,1)} + E_\mu^{(0,1)} R_\mu^{(0,1)^{(1)}} \} |0\rangle \tag{3.63}$$

$$\langle 0 | \{ \bar{R}_\mu^{(0,1)^{(1)}} R_\mu^{(0,1)} + \bar{R}_\mu^{(0,1)} R_\mu^{(0,1)^{(1)}} \} |0\rangle = 0 \tag{3.64}$$

Eqs. (3.63) and (3.64) generates sufficient number of equations for solving $E_\mu^{(0,1)^{(1)}}$ and $R_\mu^{(0,1)^{(1)}}$. Once the eigenvector derivatives for selectively chosen states are obtained, they can be used to extract S amplitude derivatives. Rewriting Eq. (3.34) as,

$$ZV_O = V \tag{3.65}$$

We expand above Eq. in terms of S amplitudes and eigenvector coefficients as,

$$-\sum_K S_{ji}^{ka} . r_k(\mu) = r_{ji}^a(\mu) \tag{3.66}$$

$$-\sum_K S_l^k . r_k(\mu) = r_l(\mu) \tag{3.67}$$

Differentiating above Eqs (3.66) and (3.67), we obtain,

$$-\sum_K \{ S_{ji}^{ka^{(1)}} . r_k(\mu) + S_{ji}^{ka} . r_k^{(1)}(\mu) \} = r^{(1)}{}_{ji}^a(\mu) \tag{3.68}$$

$$-\sum_K \{ S_l^{k^{(1)}} . r_k(\mu) + S_l^k . r_k^{(1)}(\mu) \} = r_l^{(1)}(\mu) \tag{3.69}$$

Where k and l are active and inactive hole orbital's respectively, μ is a specific eigenvector and $r_i^{(1)}$, $r^{(1)}{}_{ji}^{a}$ are the 1h and 2h1p coefficients of eigenvector derivative $R_\mu^{(0,1)^{(1)}}$. Analogously cluster amplitude derivative for (1, 0) sector can also be obtained.

After obtaining the cluster amplitude derivatives for (0, 0), (0, 1) and (1, 0) sectors, intermediate Hamiltonian derivative for (1, 1) sector can be explicitly determined as,

$$H_{int}^{(1,1)^{(1)}} = [(H_N^{(1)}e^T)_c(1+Y) + (\bar{H}_N T^{(1)})_c(1+Y^{(1,1)}) + \bar{H}_N Y^{(1,1)^{(1)}}] \tag{3.70}$$

With,

$$Y^{(1,1)^{(1)}} = \{S_2^{(0,1)^{(1)}} + S_2^{(1,0)^{(1)}} + S_1^{(0,1)^{(1)}}S_2^{(1,0)} + S_1^{(0,1)}S_2^{(1,0)^{(1)}}$$

$$+ S_1^{(1,0)^{(1)}}S_2^{(0,1)} + S_1^{(1,0)}S_2^{(0,1)^{(1)}} + S_2^{(0,1)^{(1)}}S_2^{(1,0)} + S_2^{(0,1)}S_2^{(1,0)^{(1)}}\}P_M^{(1,1)} \tag{3.71}$$

Analogous to the Eqs given by (3.61)-(3.64) for (0, 1) sector, $E_\mu^{(1,1)^{(1)}}$ and $R_\mu^{(1,1)^{(1)}}$ of (1, 1) sector can also be obtained. The only quantity which is still to be determined for evaluation of up to 2nd order energy derivative for (1, 1) sector of Fock space is $L_\mu^{(1,1)^{(1)}}$, which can be easily obtained by using the bi-orthonormality condition as,

$$\langle 0|L_\mu^{(1,1)}R_\mu^{(1,1)}|0\rangle = 1 \tag{3.72}$$

$$\langle 0|\{L_\mu^{(1,1)^{(1)}}R_\mu^{(1,1)} + L_\mu^{(1,1)}R_\mu^{(1,1)^{(1)}}\}|0\rangle = 0 \tag{3.73}$$

Once all the quantities required are solved, the 1st and 2nd order energy derivatives can be obtained through Eqs. (3.50) and (3.60).

The final step towards the evaluation of 1st order energy derivative is the insertion of $H^{(1)}$ in the Eq. (3.50). The form of $H^{(1)}$ depends on the nature of external perturbation. When electric response properties are considered, external electric

field interacting with molecular dipole operator leads to simple one body perturbation when orbital relaxation effects are neglected. In the case of geometric perturbation which leads to gradient of potential energy surface, both one and two body part of $H^{(1)}$ has to be considered. In fact, orbital relaxation effects must be considered even in the case of external electric field perturbation, as in practice orbital relaxation effects are not negligible in many cases.

Effect of orbital relaxation for first order energy derivative can be included in two possible ways. One way is to directly solve for $H^{(1)}$ for each mode of perturbation as given below.

$$
\begin{aligned}
H^{(1)} &= F^{(1)} + V^{(1)} = [dH(\lambda)/d\lambda]_{\lambda=0} \\
&= \sum f_{pq}^{(1)} . \{p^+ q\} + 1/4 \sum < pq \parallel rs >^{(1)} . \{p^+ q^+ sr\}
\end{aligned}
\tag{3.74}
$$

Where $F^{(1)}$ and $V^{(1)}$ are the one and two body Hamiltonian derivatives respectively and p, q, r and s are the molecular orbital's. In order to obtain the first order Hamiltonian derivatives, one and two electron part of Hamiltonian in AO basis along with MO coefficient and the MO coefficient derivatives are required. MO coefficient derivatives can be obtained by solving coupled perturbed Hartree Fock (CPHF) equation. The detailed procedure and working equations are well described at several places [89-91]. The advantage of direct evaluation of perturbation dependent first order derivative quantities is that it is independent of the parameters of FSMRCC and the state considered. This approach is useful only for the cases with lesser modes of perturbation as in the case of electric field perturbation. The second approach is to follow a Z-vector like method, as described by Salter and co-workers [91], which eliminates the perturbation dependent first order derivative quantities with the cost of solving a linear equation which is independent of external perturbation. This approach is quite suitable for the evaluation of molecular gradient where the number of modes of perturbation is significantly large. An obvious advantage of this approach is the

perturbation independence. However, the complication arises due to the fact that the quantities defining the Z-vector like equations are dependent of all the parameters of FSMRCC including the target state and Λ. The second approach can be generalized for including the orbital response quantities for second order properties. This can be done by extending the Lagrangian functional through inclusion of orbital response constraints, as shown by Helgaker and co-workers in SRCC [70, 92] and also by Krylov and co-workers in spin flip equation of motion coupled cluster (SF-EOMCC) [72].

It is important here to mention that in the implementation of first order properties through SRCC Z-vector method or LMA approach, further efficiency has been achieved by contracting the effective CC density matrix with $H^{(1)}$. Using Λ and T, effective CC density matrix [91] is constructed. As suggested by Rice and Amos [93], this contraction is efficiently carried out in atomic orbital (AO) basis, which avoids the transformation of $H^{(1)}$ into MO basis for each modes of perturbation. This is carried out by a single back transformation of effective CC density matrix from MO to AO basis. The same strategy can be followed here also. Using Eq. (3.50) one can construct state dependent effective IHFSMRCC density matrix.

It is desirable to investigate the interconnections between the energy derivative formulations through EH and IH approaches of FSMRCC theory. For detailed discussion about energy derivatives through LMA approach in EHFSMRCC, we refer to [78]. For the purpose of comparative analysis we choose the Lagrangian of EHFSMRCC as our reference. The form of Lagrangian in effective Hamiltonian formulation is given by,

$$\Im\{H_{eff}\} = \left\langle 0 \left| \tilde{C}^{(1,1)} H_{N,eff}^{(1,1)} C^{(1,1)} \right| 0 \right\rangle + P_M^{(1,1)} \Lambda^{(1,1)} P_I^{(1,1)} [H_N \Omega - \Omega H_{N,eff}] P_M^{(1,1)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [H_N \Omega - \Omega H_{N,eff}] P_M^{(1,0)}$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [H_N \Omega - \Omega H_{N,eff}] P_M^{(0,1)}$$

$$+P_M^{(0,0)}\Lambda^{(0,0)}P_I^{(0,0)}\bar{H}_N P_M^{(0,0)} - E_\mu[\langle 0|\tilde{C}^{(1,1)}C^{(1,1)}|0\rangle - 1]$$

(3.75)

Comparing the form of Lagrangian in both of the formulations, we find that there are essentially two basic differences between them. One is in IHFSMRCC Lagrangian, effective Hamiltonian has been replaced by intermediate Hamiltonian along with their corresponding eigenvectors and the second is the constraint pre multiplied by $\Lambda^{(1,1)}$ vanishes which is the consequence of the fact that IH matrix for (1, 1) sector is independent of the cluster amplitudes of (1, 1) sector. As previously mentioned, each term present in the expression of $\Im$ has to be differentiated with respect to cluster operator of various sectors in order to obtain the equations for Λ vectors. This is usually employed by using efficient diagrammatic technique which is well described at several places [78]. As the second term of the RHS of Eq. (3.75) vanishes in LMA-IHFSMRCC approach, it reduces the computational effort by reducing the number of diagrams to be coded in comparison to LMA-EHFSMRCC approach.

At last, it is noteworthy to mention that the present IH formulation of FSMRCC does not introduce a different level of theory, but it provides an alternative way to reach the solution of EH formulation of FSMRCC in numerically stable and cost effective manner. As a consequence of this, both the formulations practically remain connected to each other at the level of energy derivative also and one can switch from one formulation to the other, if required. For example, one can perform the excitation energy calculation through IHFSMRCC and obtain the cluster operators from the eigenvectors to construct the EH matrix for any further consideration. This approach has already been exploited by Meissner and their co-workers to include the effect of partial non iterative triples in excitation energy within IH framework [94, 95]. Similar strategy can be utilized for energy derivative also. For this, one can completely proceed for energy derivative via LMA-EHFSMRCC approach after solving the cluster operators of each sector

through IHFSMRCC with larger model space. Although this does not lead to computationally efficient way to obtain the energy derivative, it provides an obvious example where both of the formulations can be merged together. Similarly the cluster response quantities also can be evaluated by both of the formulations equivalently.

3.6 Summery and conclusions:

We have presented a formulation for analytic energy derivative using Lagrange multiplier approach through intermediate Hamiltonian formulation of FSMRCC. This formulation has been used to derive the explicit generic expressions for first and second order energy derivatives. In this work we have particularly used the IH-FSMRCC formulation of Meissner for evaluation of energy derivatives. Though equations are derived for (1, 1) sector of FSMRCC, its extension for any sector, in which effective Hamiltonian is explicitly defined in terms of wave operator, (which is usually the case of CMS and some of the special classes of incomplete model spaces like (1, 1) sector) is straight forward. Effective Hamiltonian based FSMRCC theory suffers from intruder state problem when the model space is enlarged. Its reformulation through IH technique provides a numerically stable and cost effective way to obtain the roots via direct diagonalization procedure. Extension of LMA approach for IH-FSMRCC energy derivative opens a path for evaluation of excited state properties with larger model space. This not only provides more number of states, but also in many cases significantly improves the correlation effect which is essential for accurate treatment of properties. In IH-FSMRCC excitation energy calculation, final diagonalization takes place in 1h1p space. This allows one to perform the calculations for excitation energy as well as excited state properties using bigger basis sets. In IH formulation of FSMRCC cluster amplitudes for highest sector (in this case (1, 1) sector) are decoupled from the eigenvalue problem. Consequently, in comparison to effective Hamiltonian based energy derivative, IHFSMRCC

energy derivative calculations get simplified. Computational implementation of this formulation for 1st and 2nd order molecular response properties is presently under our study. It is desirable to mention here that apart from the evaluation of energy derivatives, this formulation can also be used to parameterize the left vector for a desired excited state which is essentially required if one is interested in expectation value properties like electronic transition dipole moment (ETDM). Very recently, this strategy has been used by Pal and coworkers for evaluation of ETDM within effective Hamiltonian framework [96]. Calculation of electronic TDM within IHFSMRCC framework can also be seen as a possible application of our present work, apart from evaluation of energy derivatives. Finally, in our opinion, this formulation may emerge as an attractive candidate for accurate and efficient evaluation of excited state properties in routine applications, which is probably one of the most essential criteria for establishing a theoretical framework as a method of first choice [97].

Appendix 3.A

Elimination of derivative cluster amplitudes in first order response properties:

Differentiating the Lagrangian functional (defined through Eq. (3.40)), with respect to external perturbation as,

$$\Im^{(1)} = \langle 0 | [L^{(1,1)^{(1)}} H_{Int}^{(1,1)} R^{(1,1)} + L^{(1,1)} H_{Int}^{(1,1)^{(1)}} R^{(1,1)} + L^{(1,1)} H_{Int}^{(1,1)} R^{(1,1)^{(1)}}] | 0 \rangle$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)^{(1)}} P_I^{(0,1)} (1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)}) P_M^{(0,1)}$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]^{(1)} P_M^{(0,1)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)^{(1)}} P_I^{(1,0)} (1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)}) P_M^{(1,0)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]^{(1)} P_M^{(1,0)}$$

$$+ P_M^{(0,0)} \Lambda^{(0,0)^{(1)}} P_I^{(0,0)} \bar{H}_N P_M^{(0,0)} + P_M^{(0,0)} \Lambda^{(0,0)} P_I^{(0,0)} [\bar{H}_N]^{(1)} P_M^{(0,0)}$$

$$- E_\mu^{(1)} [\langle 0 | L^{(1,1)} R^{(1,1)} | 0 \rangle - 1] - E_\mu \langle 0 | [L^{(1,1)^{(1)}} R^{(1,1)} + L^{(1,1)} R^{(1,1)^{(1)}}] | 0 \rangle \qquad (3.A1)$$

The 1st , 3rd , 10th and 11th terms of the RHS of the above equation vanish collectively due to fulfillment of bi-orthonormality condition and Eigen value equations of desired state, while 4th, 6th and 8th terms vanish individually because of satisfying FSMRCC equations of (0,1), (1,0) and (0,0) sectors respectively. After these simplifications, we get,

$$\Im^{(1)} = \langle 0 | L^{(1,1)} [H_{Int}^{(1,1)}]^{(1)}_{H_N \to H_N^{(1)}} R^{(1,1)} | 0 \rangle$$
$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]^{(1)}_{H_N \to H_N^{(1)}} P_M^{(0,1)}$$
$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]^{(1)}_{H_N \to H_N^{(1)}} P_M^{(1,0)}$$
$$+ P_M^{(0,0)} \Lambda^{(0,0)} P_I^{(0,0)} [\bar{H}_N]^{(1)}_{H_N \to H_N^{(1)}} P_M^{(0,0)} + W[\{X^{(0,1)^{(1)}}, X^{(1,0)^{(1)}}, T^{(0,0)^{(1)}}\}] \qquad (3.A2)$$

Where, $W[\{X^{(0,1)^{(1)}}, X^{(1,0)^{(1)}}, T^{(0,0)^{(1)}}\}]$ represents the additional terms collectively, containing the response of cluster amplitudes of all the sectors of Fock space, except the highest one. Subscript $H_N \to H_N^{(1)}$ refers to the replacement of zeroth-order Hamiltonian H_N by field perturbation operator $H_N^{(1)}$ in expressions in square bracket. It is almost trivial to show that, $W[\{X^{(0,1)^{(1)}}, X^{(1,0)^{(1)}}, T^{(0,0)^{(1)}}\}]$ can be written as,

$$W = \left(\frac{\partial \mathfrak{I}}{\partial S^{(0,1)}}\right) S^{(0,1)^{(1)}} + \left(\frac{\partial \mathfrak{I}}{\partial S^{(1,0)}}\right) S^{(1,0)^{(1)}} + \left(\frac{\partial \mathfrak{I}}{\partial T^{(0,0)}}\right) T^{(0,0)^{(1)}}$$

(3.A3)

which is zero because equations for Λ of (0,1), (1,0) and (0,0) sectors are satisfied, see Eqs. (3.47), (3.48) and (3.49). Hence $\mathfrak{I}_{opt}^{(1)}$ is given by the remaining terms of the Eq. (3.A2).

Appendix 3.B

Elimination of derivative cluster amplitudes in second order response properties:

Differentiating the Eq. (3.A1) w.r.t. the external perturbation as,

$$\Im^{(2)} = \left\langle 0\right|\{L^{(1,1)^{(2)}} H_{Int}^{(1,1)} R^{(1,1)} + L^{(1,1)^{(1)}} H_{Int}^{(1,1)^{(1)}} R^{(1,1)} + L^{(1,1)^{(1)}} H_{Int}^{(1,1)} R^{(1,1)^{(1)}}$$

$$+ L^{(1,1)^{(1)}} H_{Int}^{(1,1)^{(1)}} R^{(1,1)} + L^{(1,1)} H_{Int}^{(1,1)^{(2)}} R^{(1,1)} + L^{(1,1)} H_{Int}^{(1,1)^{(1)}} R^{(1,1)^{(1)}}$$

$$+ L^{(1,1)^{(1)}} H_{Int}^{(1,1)} R^{(1,1)^{(1)}} + L^{(1,1)} H_{Int}^{(1,1)^{(1)}} R^{(1,1)^{(1)}} + L^{(1,1)} H_{Int}^{(1,1)} R^{(1,1)^{(2)}} \}\left|0\right\rangle$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)^{(2)}} P_I^{(0,1)} (1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)}) P_M^{(0,1)}$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]^{(2)} P_M^{(0,1)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)^{(2)}} P_I^{(1,0)} (1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)}) P_M^{(1,0)}$$

$$+ 2 P_M^{(1,0)} \Lambda^{(1,0)^{(1)}} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]^{(1)} P_M^{(1,0)}$$

$$+ P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]^{(2)} P_M^{(1,0)}$$

$$+ P_M^{(0,0)} \Lambda^{(0,0)^{(2)}} P_I^{(0,0)} \bar{H}_N P_M^{(0,0)} + 2 P_M^{(0,0)} \Lambda^{(0,0)^{(1)}} P_I^{(0,0)} [\bar{H}_N]^{(1)} P_M^{(0,0)}$$

$$+ P_M^{(0,0)} \Lambda^{(0,0)} P_I^{(0,0)} [\bar{H}_N]^{(2)} P_M^{(0,0)} - E_\mu^{(2)} (\left\langle 0\right| L^{(1,1)} R^{(1,1)} - 1)\left|0\right\rangle$$

$$- 2 E_\mu^{(1)} \left\langle 0\right| (L^{(1,1)^{(1)}} R^{(1,1)} + L^{(1,1)} R^{(1,1)^{(1)}})\left|0\right\rangle$$

$$- E_\mu \left\langle 0\right| (L^{(1,1)^{(2)}} R^{(1,1)} + L^{(1,1)^{(1)}} R^{(1,1)^{(1)}} + L^{(1,1)} R^{(1,1)^{(2)}})\left|0\right\rangle \tag{3.B1}$$

After lots of simplifications the above functional can be written as,

$$\Im^{(2)} = \left\langle 0\right| L^{(1,1)} H_{Int}^{(1,1)^{(2)}} R^{(1,1)} \left|0\right\rangle + P_M^{(0,0)} \Lambda^{(0,0)} P_I^{(0,0)} [\bar{H}_N]^{(2)} P_M^{(0,0)}$$

$$+P_M^{(0,1)}\Lambda^{(0,1)}P_I^{(0,1)}[(1-X^{(0,1)})\bar{H}_N(1+X^{(0,1)})]^{(2)}P_M^{(0,1)}$$

$$+P_M^{(1,0)}\Lambda^{(1,0)}P_I^{(1,0)}[(1-X^{(1,0)})\bar{H}_N(1+X^{(1,0)})]^{(2)}P_M^{(1,0)}$$

$$-2(\langle 0|L^{(1,1)^{(1)}}H_{Int}^{(1,1)}R^{(1,1)^{(1)}}|0\rangle-E_\mu\langle 0|L^{(1,1)^{(1)}}R^{(1,1)^{(1)}}|0\rangle) \tag{3.B2}$$

The final step towards the evaluation of second order energy derivatives is to show the elimination of second order derivatives of cluster amplitudes i. e. $X^{(2)}$ and $T^{(2)}$ from the above functional. Let us consider each term of Eq. (3.B2), except the last one, separately as,

$$\langle 0|L^{(1,1)}H_{Int}^{(1,1)^{(2)}}R^{(1,1)}|0\rangle = A \tag{3.B3}$$

$$P_M^{(0,0)}\Lambda^{(0,0)}P_I^{(0,0)}[\bar{H}_N]^{(2)}P_M^{(0,0)} = B \tag{3.B4}$$

$$P_M^{(0,1)}\Lambda^{(0,1)}P_I^{(0,1)}[(1-X^{(0,1)})\bar{H}_N(1+X^{(0,1)})]^{(2)}P_M^{(0,1)} = C \tag{3.B5}$$

$$P_M^{(1,0)}\Lambda^{(1,0)}P_I^{(1,0)}[(1-X^{(1,0)})\bar{H}_N(1+X^{(1,0)})]^{(2)}P_M^{(1,0)} = D \tag{3.B6}$$

A can be expanded as,

$$A = \langle 0|[(H_N^{(2)}e^{(T)})_c(1+Y)+2((H_N^{(1)}e^{(T)})_cT^{(1)})_c(1+Y)+((\bar{H}_NT^{(1)})_cT^{(1)})_c(1+Y)$$

$$+2\bar{H}_N^{(1)}Y^{(1)}+(\bar{H}_NT^{(2)})_c(1+Y)+\bar{H}_NY^{(2)}]R^{(1,1)}|0\rangle \tag{3.B7}$$

The last two terms of the above expression of A, have the second order cluster response terms. Let us denote these terms collectively as A1 and rest of the terms as A2. Hence,

A=A1+A2 $\tag{3.B8}$

It is again obvious to show that A1 can be written as,

$$A1 = \langle 0|L^{(1,1)}[[H_{Int}^{(1,1)}]_{S^{(0,1)}}^{(1)}S^{(0,1)^{(2)}}+[H_{Int}^{(1,1)}]_{S^{(1,0)}}^{(1)}S^{(1,0)^{(2)}}+[H_{Int}^{(1,1)}]_T^{(1)}T^{(2)}R^{(1,1)}|0\rangle \tag{3.B9}$$

Analogously the second order cluster response containing terms of the B, C and D also can be written as,

$$B1 = P_M^{(0,0)} \Lambda^{(0,0)} P_I^{(0,0)} [\bar{H}_N]_T^{(1)} T^{(2)} P_M^{(0,0)} \tag{3.B10}$$

$$C1 = P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]_{S^{(0,1)}}^{(1)} S^{(0,1)^{(2)}} P_M^{(0,1)}$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]_T^{(1)} T^{(2)} P_M^{(0,1)} \tag{3.B11}$$

$$D1 = P_M^{(1,0)} \Lambda^{(1,0)} P_I^{(1,0)} [(1 - X^{(1,0)}) \bar{H}_N (1 + X^{(1,0)})]_{S^{(1,0)}}^{(1)} S^{(1,0)^{(2)}} P_M^{(1,0)}$$

$$+ P_M^{(0,1)} \Lambda^{(0,1)} P_I^{(0,1)} [(1 - X^{(0,1)}) \bar{H}_N (1 + X^{(0,1)})]_T^{(1)} T^{(2)} P_M^{(0,1)} \tag{3.B12}$$

Adding the terms A1, B1, C1 and D1 and collecting the second order cluster response quantities of each sectors separately, we can write,

$$A1 + B1 + C1 + D1 = V \, (let) \tag{3.B13}$$

$$V = \left(\frac{\partial \Im}{\partial S^{(0,1)}} \right) S^{(0,1)^{(2)}} + \left(\frac{\partial \Im}{\partial S^{(1,0)}} \right) S^{(1,0)^{(2)}} + \left(\frac{\partial \Im}{\partial T^{(0,0)}} \right) T^{(2)}$$

$$\tag{3.B14}$$

This is again zero due to Eqs. (3.47), (3.48) and (3.49). Hence, $\Im_{opt}^{(2)}$ is given by the remaining terms of the Eq. (3.B2).

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Chapter 4

Electronic transition dipole moments and oscillator strengths through intermediate Hamiltonian formulation of Fock space multi-reference coupled cluster theory

In this chapter, we have calculated electronic transition dipole moment (ETDM) through intermediate Hamiltonian formulation of Fock space multi-reference coupled-cluster (IHFSMRCC) theory, which measures the absorption intensities. ETDM can be directly obtained through matrix element of one particle electric perturbation operator between ground and excited states. A Lagrange multiplier approach has been used to parameterize the left vector of both ground and excited states, while the right vector of excited state is obtained through eigenvalue structure of intermediate Hamiltonian matrix. Apart from ETDM, excitation energies have also been calculated through IHFSMRCC in order to relate ETDM to oscillator strength using dipole length approximation. We have presented the transition dipole moments and oscillator strengths of a few molecules and compared our results with values obtained through equation of motion coupled-cluster (EOMCC) method.

4.1 Introduction:

Electronic transition dipole moments (ETDM) can determine the absorption intensity of electronic transition, extinction coefficient and fluorescence lifetime etc [1, 2]. It can be helpful in understanding the energy transfer rate and optical spectra [3]. Similar to the case of electronic dipole moment, the ETDM is very sensitive to the basis set as well as the correlation effects. Hence, it can provide a good test for validating the accuracy of an electronic structure theory. ETDM are defined as a matrix elements of electronic dipole operator between two different eigen states. ETDM can be directly related to experimental observable like oscillator strength using the dipole length approximation [4].

Despite the fact that ETDM are of great general interest, evaluating and relating them to experimentally measurable quantity is practically not very straightforward. This is due to the fact that ETDM are extremely sensitive toward the quality of wave function [5]. Hence, we require a very accurate description of wave function in order to evaluate the ETDM. Coupled-cluster (CC) methods [6] have the potential to provide the wave function with desired accuracy to serve this purpose. We have already discussed in detail about the development of SRCC methods [7-13] and its extension to MR situations leading to FSMRCC [14-21] methods, in previous chapters of this thesis.

Olsen et al. calculated the excitation energy and electronic transition moments in multi configuration linear response (MCLR) approach [22]. Stanton and Bartlett [23] used a systematic bi-orthogonal approach for calculating ETDM through EOMCC method. Jorgensen and co-workers developed formalism for size intensive transition moment through coupled cluster linear response (CCLR) [24]. Calculation of expectation values and transition moments by coupled cluster theory in general, was described in detail by Prasad [25]. Christiansen et al [26] implemented the integral-direct frequency dependent polarizabilities and transition

probabilities in coupled cluster framework. Transition moments were calculated by Hattig and Kohn [27] within resolution of identity CC2 (RICC2) approximation. This was later extended by Kohn and Pabst [28], who implemented the transition moment between excited states. Stolarczyk and Monkhorst [29] formulated expectation value and transition moments also in their early work within the generalized CC framework, which was later implemented by Barysz *et al* [30, 31] for ETDM and OS through FSMRCC method. Very recently, Pal and co-workers also implemented for ETDM and OS in FSMRCC framework using a different approach [32]. Analogous to the case of left vector of ground state, they used a Lagrange multiplier approach in order to parameterize the left vector of excited states for calculating size intensive transition moments.

As we discussed in chapter 3, the traditional effective Hamiltonian based FSMRCC [14-21] theory suffers from intruder states [33, 34]. The intermediate Hamiltonian [35-48] formulation of Meissner [36] provides an alternative way to reach the convergence in a more efficient manner with larger model space. This not only helps one to obtain the excited state properties for more number of states, but also, in several cases, significantly improves the correlation effects. We also extended the LMA in IHFSMRCC [49] formulation of Meissner for energy derivatives, in order to obtain excited state properties for desired number of states with bigger basis sets and larger model space in numerically stable and cost effective way. Hence, an obvious next step is to computationally implement the LMA-IHFSMRCC formulation for evaluation of excited state properties. We have chosen ETDM and OS as the excited state properties in order to extend the scope and applicability of IHFSMRCC method.

This chapter is organized as follows. In section 4.2, we will discuss in brief the theory of IHFSMRCC required for deriving the working equation for ETDM and OS. Section 4.3 is dedicated to the results and discussion. Finally we have given some concluding remarks in section 4.4.

4.2 Electronic transition dipole moment through IHFSMRCC

A general approach to evaluate transition moments within generalized CC framework has been developed by Stolarczyk and Monkhorst [29]. We have followed the same general approach and extended it for the IH formulation of FSMRCC [36-45].

Hamiltonian of a molecular system interacting with external electric field is given by,

$$\hat{H}(F) = \hat{H}(0) + \hat{\mu}.F \tag{4.1}$$

Where, $H(0)$ is the Hamiltonian without external perturbation, $\hat{\mu}$ is the one electron electric perturbation operator and F is the field strength.

Electronic transition dipole moment between two states Ψ_p and Ψ_q is defined as the matrix elements of electric dipole operator $\hat{\mu}$ between these states and given as

$$\mu_p^q = \left\langle \Psi_p \left| \hat{\mu} \right| \Psi_q \right\rangle \tag{4.2}$$

Where, Ψ_p and Ψ_q ($p \neq q$) are the orthonormal eigenstates of the Hamiltonian operator of molecular system. Due to non-Hermitian nature of normal coupled cluster theory, the electronic transition dipole moment is defined as a geometric mean of μ_p^q and μ_q^p. Hence, ETDM is given more precisely as,

$$d_{pq} = \sqrt{\left\langle \Psi_p \left| \hat{\mu} \right| \Psi_q \right\rangle \left\langle \Psi_q \left| \hat{\mu} \right| \Psi_p \right\rangle} \tag{4.3}$$

In this present chapter work, we have considered the electronic transition dipole moments from ground state to a few excited states. Hence,

$$\left\langle \Psi_p \right| = \left\langle \Psi_g \right| \text{ and } \left| \Psi_p \right\rangle = \left| \Psi_g \right\rangle \tag{4.4}$$

And,

$$\left\langle \Psi_q \right| = \left\langle \Psi_{ex} \right| \text{ and } \left| \Psi_q \right\rangle = \left| \Psi_{ex} \right\rangle \tag{4.5}$$

As we discussed in chapter 3, ground state is given by the standard CC equation in IHFSMRCC framework and intermediate Hamiltonian for (1, 1) sector of FSMRCC theory is given by,

$$H_{Int}^{(1,1)} = P_O^{(1,1)} \overline{H_N} (1 + Y^{(1,1)}) P_O^{(1,1)} \tag{4.6}$$

Where,

$$Y^{(1,1)} = Q_O^{(1,1)} \{ S_2^{(0,1)} + S_2^{(1,0)} + S_1^{(0,1)} S_2^{(1,0)} + S_1^{(1,0)} S_2^{(0,1)} + S_2^{(0,1)} S_2^{(1,0)} \} P_M^{(1,1)} \tag{4.7}$$

Exploiting the eigenvalue structure of Eq. (4.6), right vectors for the ground and excited states are given by,

$$\left| \Psi_g \right\rangle = e^T \left| \Phi_0 \right\rangle \tag{4.8}$$

$$\left| \Psi_{ex} \right\rangle = e^T (1 + Y^{(1,1)}) R^{(1,1)} \left| \Phi_0 \right\rangle \tag{4.9}$$

It is the well established fact that using an extra set of de-excitation amplitudes, the left vector for the ground state can be parameterized [23, 24] as,

$$\left\langle \Psi_g \right| = \left\langle \Phi_0 \right| (1 + \Lambda) e^{-T} \tag{4.10}$$

Analogous to the case of ground state, using Lagrange multiplier approach (LMA), left vector for the excited state within IHFSMRCC framework can also be parameterized as,

$$\left\langle \Psi_{ex} \right| = \left\langle \Phi_0 \right| L^{(1,1)} (1 + \tilde{\Lambda}) e^{-Y^{(1,1)}} e^{-T} \tag{4.11}$$

Where, $\tilde{\Lambda} = (\Lambda^{(0,0)} + \Lambda^{(0,1)} + \Lambda^{(1,0)})$ \hfill (4.12)

A detailed description of LMA-IHFSMRCC [49] approach and the way to solve the equations for Λ vectors for (1, 1) sector has already been given in chapter 3. A similar LMA approach within effective Hamiltonian (EH) FSMRCC method has also been developed and recently applied for ETDM by Pal and co-workers [32].

The electronic transition dipole moment through IHFSMRCC is finally given by,

$$d_{pq} = \sqrt{[\langle \Phi_0 | (1+\Lambda)(\hat{\mu}e^T)_c (1+Y^{(1,1)}) R^{(1,1)} | \Phi_0 \rangle \langle \Phi_0 | L^{(1,1)}(1+\tilde{\Lambda})e^{-Y^{(1,1)}} (\hat{\mu}e^T)_c | \Phi_0 \rangle]} \qquad (4.13)$$

This ETDM is not the experimentally measurable quantity. Square of this ETDM is defined as the dipole strength.

$$\text{Dipole strength} = |d_{pq}|^2 \qquad (4.14)$$

Finally, this dipole strength can be directly related to the oscillator strength, which is an experimental observable. The oscillator strength in dipole length approximation [4] is given as,

$$f_{pq} = \frac{2}{3}\Delta E |d_{pq}|^2 \qquad (4.15)$$

Where ΔE denotes the excitation energy which can be obtained through IHFSMRCC method.

4.3 Computational Results and discussions:

The computational procedure for getting excitation energy and electronic transition dipole moment through IHFSMRCC involves the following steps. We have solved the ground state CCSD equations and obtained T amplitudes after solving restricted Hartree-Fock equation. For the efficient computational implementation, one and two body parts of $\bar{H}_N$ are constructed with the help of T and stored in the disk while three body part of $\bar{H}_N$ is being constructed instantly, whenever required. These $\bar{H}_N$ intermediates are used to solve the IH matrix

eigenvalue problem for (0, 1) and (1, 0) sectors. As the dimension of IH matrix for (0, 1) and (1, 0) sectors is very large, an efficient diagonalization routine has to be used for solving the eigenvalue problems for few of the selected roots. In practice this is followed by Nakatsuji-Hirao algorithm [50] of non symmetric matrices, which is the generalization of Davidson algorithm [51] for symmetric matrices. Once the eigenvalue problem is solved, eigenvectors for selective roots are transformed into the $S^{(0,1)}$ and $S^{(1,0)}$. These S amplitudes are used to construct the IH matrix for (1, 1) sector and solve the eigenvalue problem. After getting the eigen value and eigen vector of a particular excited state, we solve the equation for lambda vectors of (0, 1) and (1, 0) sectors and then of (0, 0) sector. The detailed working equation for solving lambda vectors through IH formulation of FSMRCC is given and discussed in chapter 3. These lambda vectors are directly used to parameterize left vector of excited state as given in Eq. 4.11. Finally, ETDM between ground and that particular excited state is calculated through Eq. 4.13. We have used the Goldstone diagrammatic technique for matrix element evaluation throughout our work.

We have chosen three molecules, CH^+, H_2O, and HCHO for our test calculation. Excited states of all three molecules have been calculated at the equilibrium geometry. Hence these are the vertical excitation energy. The electronic transition dipole moments are evaluated under the Frank Condon principle of fixed nuclear framework. The scaling of these calculations is N^6. We have benchmarked our calculations with full CI results available for the CH^+ molecule in a basis given in reference 22. For the H_2O molecules, we have performed our test calculation in cc-pVTZ and cc-pVQZ basis sets. For the HCHO molecule, the calculation has been performed in a single cc-pVDZ basis set. We have chosen our test systems, basis sets and equilibrium geometries identical with given in references 22 and 32, in order to directly compare our results with other existing methods.

4.3.1 CH$^+$ molecule:

The ground state electronic configuration of CH$^+$ is $1\sigma^2 2\sigma^2 3\sigma^2$ which is chosen as vacuum. In our calculation the equilibrium bond length of CH$^+$ is taken to be 2.13713 a.u. Due to interaction of $1\sigma^2 2\sigma^2 3\sigma^2$ and $1\sigma^2 2\sigma^2 1\pi^2$ electronic configurations, there is a large non-dynamic correlation in the ground state itself. We have chosen 2 occupied and 10 virtual orbitals to be active and reported the transition moments between ground state and some of the excited states dominated by the single active hole-particle excitation in table 4.1. For the particular state 1 (dominated by $3\sigma \rightarrow 1\pi$ transition), we have compared our results with three other methods namely FCI, EOMCC and FSCC*. For the details regarding these calculations, we refer to 22, 31 and 32. We observe that ETDM, transition energy and hence, the oscillator strength values obtained through our IHFSMRCC method are close to FCI values. For state 2 and state 3, our results agree well with the EOMCC values.

Table 4.1: Excitation energies, transition moments, and oscillator strengths of CH$^+$ molecule from its ground state to a few excited states

CH$^+$		State-1 $(3\sigma \rightarrow 1\pi)$			State-2 $(3\sigma \rightarrow 4\sigma)$		State-3 $(3\sigma \rightarrow 5\sigma)$	
	IHFSCC	EOMCC[a]	FCI[b]	FSCC[c]	IHFSCC	EOMCC[a]	IHFSCC	EOMCC[a]
EE	0.1190	0.1198	0.1187	0.1191	0.5012	0.4990	0.6492	0.6544
TDM	0.301	0.306	0.299	0.243	1.025	1.036	0.186	0.176
OS	0.0072	0.0076	0.0070	0.0046	0.3510	0.3571	0.0150	0.0135

[a] see reference 32, [b] see reference 22, [c] see reference 31

4.3.2 H₂O molecule:

The equilibrium O-H bond length and H-O-H bond angle is taken to be 1.809 a.u. and 104.52^o respectively. Restricted Hartree-Fock determinant is chosen as Fermi vacuum which is given by $1a_1^2 2a_1^2 1b_1^2 3a_1^2 1b_2^2$ electronic configuration. We have chosen 4 occupied and 12 unoccupied orbitals to be active in our model space all the for water molecule in cc-pVTZ and cc-pVQZ basis. It is clear from the table 4.2 and 4.3 that as we move from cc-pVTZ to cc-pVQZ basis, both the EOMCC and IHFSCC values of excitation energy are decreased. Our IHFSMRCC values agree well with corresponding EOMCC values. It is clear from table 4.2 and 4.3 that ETDM values obtained through IHFSMRCC differ with EOMCC values within the range of 0.01a.u. to 0.04 a.u.. The transition dipole moment values obtained through IHFSMRCC method is slightly lower than that of EOMCC values for all the states in both the basis sets consistently. The experimental oscillator strength value is reported as 0.041 a.u. for state 1. The convergence towards experimental value for state 1 has been observed as we move from cc-pVTZ to cc-pVQZ basis.

Table 4.2: Excitation energies, transition moments, and oscillator strengths of H₂O molecule from its ground state to a few excited states in cc-pVTZ basis.

H₂O in cc-pVTZ basis		State-1 $(1b_2 \rightarrow 4a_1)$	State-2 $(1b_1 \rightarrow 2b_1)$	State-3 $(3a_1 \rightarrow 4a_1)$	State-4 $(3a_1 \rightarrow 2b_1)$	State-5 $(1b_1 \rightarrow 4a_1)$
EE	IHFSCC	0.2959	0.6311	0.3869	0.4658	0.5309
	EOMCC[a]	0.2964	0.6302	0.3879	0.4652	0.5317
ETDM	IHFSCC	0.410	0.430	0.629	0.409	0.798
	EOMCC[a]	0.421	0.435	0.637	0.439	0.806
OS	IHFSCC	0.0331	0.0778	0.1021	0.0519	0.2254
	EOMCC[a]	0.0351	0.0795	0.1050	0.0597	0.2304

[a] see reference 32

Table 4.3: Excitation energies, transition moments, and oscillator strengths of H_2O molecule from its ground state to a few excited states in cc-pVQZ basis.

H_2O cc-pVQZ basis		State-1 $(1b_2 \rightarrow 4a_1)$	State-2 $(1b_1 \rightarrow 2b_1)$	State-3 $(3a_1 \rightarrow 4a_1)$	State-4 $(3a_1 \rightarrow 2b_1)$	State-5 $(1b_1 \rightarrow 4a_1)$
EE	IHFSCC	0.2930	0.6062	0.3821	0.4581	0.5192
	EOMCC[a]	0.2934	0.6070	0.3827	0.4574	0.5260
ETDM	IHFSCC	0.438	0.309	0.639	0.378	0.701
	EOMCC[a]	0.465	0.322	0.650	0.397	0.749
OS	IHFSCC	0.0375	0.0384	0.1039	0.0437	0.1700
	EOMCC[a]	0.0424	0.0419	0.1077	0.0480	0.1966

[a] see reference [32]

4.3.3 HCHO molecule:

The equilibrium C=O and C-H bond length and H-C-H bond angle in HCHO molecule is taken as $1.20838 \overset{o}{A}$ and $1.116351 \overset{o}{A}$ and 121.75 degrees. The ground state restricted Hartree-Fock determinant is chosen as the vacuum, which is given by $1a_1 2a_1 3a_1 4a_1 1b_2 5a_1 1b_1 2b_2$ electronic configuration. We have chosen six occupied and 10 virtual orbitals to be active. The calculation has been performed in a single cc-pVDZ basis. We observe from table 4.4 that our IHFSMRCC excitation energy, ETDM and oscillator strength values agree well with the corresponding EOMCC values for all the four states reported in table 4.4.

Table 4.4: Excitation energies, transition moments, and oscillator strengths of HCHO molecule from its ground state to a few excited states in cc-pVDZ basis.

HCHO in cc-pVDZ basis		State1 $(2b_2 \rightarrow 6a_1)$	State2 $(2b_2 \rightarrow 3b_2)$	State3 $(2b_2 \rightarrow 7a_1)$	State4 $(5a_1 \rightarrow 2b_1)$
EE	IHFSCC	0.3138	0.4165	0.4194	0.3378
	EOMCC[a]	0.3145	0.4180	0.4235	0.3494
TDM	IHFSCC	0.792	1.368	0.269	0.102
	EOMCC[a]	0.813	1.338	0.295	0.091
OS	IHFSCC	0.1311	0.5195	0.0201	0.0022
	EOMCC[a]	0.1385	0.4993	0.0245	0.0019

[a] see reference 32

4.4 Conclusions:

In this chapter, we have presented an efficient and attractive way to calculate the electronic transition moments through intermediate Hamiltonian formulation of FSMRCC theory. As the highest sector cluster amplitudes are decoupled from the eigen value problem, consequently, the highest sector Lagrange multipliers are also decoupled from the parameters of left vector of a given excited state. This helps one to achieve the computational efficiency up to a desirable extent. IH formulation of FSMRCC allows us to perform the excitation energy calculation in bigger basis set with large active space, which significantly improves the correlation effects. In our present work, we have tested our method with three test systems namely CH^+, H_2O and HCHO. Although we have found our preliminary test results to be in good agreement with corresponding EOMCC and FCI

(wherever feasible) values, some extensive calculations, with significantly larger basis, have to be performed in order to draw some discrete conclusions about the accuracy of the method. This is presently under our study and will be addressed in our future publication. Finally, in our opinion our LMA-IHFSMRCC formulation may emerge as an attractive candidate for efficient and accurate calculation of electronic transition dipole moment in future.

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Chapter 5

Some pilot applications of intermediate Hamiltonian Fock space multi-reference coupled cluster method to core excitation energy

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The Fock space multi-reference coupled cluster (FSMRCC) method provides an efficient approach for direct calculation of excitation energies. In the intermediate Hamiltonian (IH-FSMRCC) formulation, the method is free from intruder state problem and associated convergence difficulties, even for a large active space. In this paper we demonstrate that the IH-FSMRCC method with suitable chosen model space can be used   for accurate description of core excitation spectra of molecules even with Hartree-Fock orbital for the neutral molecules. We have reported the core excitation energy of three test systems H_2O, N_2 and CH_4. Unlike the EOM based method, the IH-FSMRCC does not require any special technique for convergence. Our preliminary test results show that the IHFSMRCC method with singles and doubles approximation outperforms the standard EOMEE-CCSD method.

5.1. Introduction

In chapter 2, we presented a variant of single reference coupled cluster method (CCM) [1-10] for first order ground state molecular electric response properties for closed shell molecular systems [11]. In chapter 3, we discussed in detail about FSMRCC [12-26], its reformulation through IH technique i.e. IHFSMRCC [27-42] and LMA-IHFSMRCC [43] approach. In chapter 4, we have implemented the LMA-IHFSMRCC method for efficient evaluation of electronic transition dipole moment (ETDM) and oscillator strength (OS) for closed shell molecular systems. In this chapter, we have shown few molecular applications of IHFSMRCC method for core excitation energy.

X –ray absorption spectroscopy (XAS) has emerged as an important tools for elucidation of structure of materials in recent times. The XAS is generally characterized by excitation of electron from core to virtual orbitals. Proper understanding and accurate interpretation of experimental data often requires reliable theoretical description of the phenomenon. However, theoretical description of core-excitation spectra is difficult. The large relaxation effect accompanying the excitation of core electron into the valence or Rydberg state often makes a balanced description of ground and core-excited state a complicated one.

The coupled cluster based approaches, which have been extremely successful in describing valence excitation spectra, can be used for the purpose. Existing coupled cluster (CC) approaches to core-excitations processes, namely, the open-shell electron attachment equation-of-motion coupled cluster (OS-EA-EOMCC) method [44] or its SAC-CI [45] analogue (OS-SAC-CI) approach, separate the orbital relaxation processes from the correlation effects and predict core-excitation spectra with reasonable agreement with experimental value. However, both the methods have the problems of solving the coupled cluster equation for core-

ionized state. Similar, problems also occur for solving the coupled cluster equation for maximum overlap method based EOMCC method [46-48]. Recently, Pittner and co-workers [49] have shown that the multi-reference coupled cluster (MRCC) method, even in singles and doubles approximation, can give very accurate core-excitation spectra and the method is free from the difficulties associated with standard single-reference coupled cluster method. However, the used state-specific MRCC requires two separate calculations for the ground and the excited state. On the other hand, direct difference energy based MRCC approaches calculate the excitation energy in single calculations and can be an efficient way for calculation of core-excitation energy. The Fock space multi-reference CC (FSMRCC) [12-26] method is well known for its ability to give accurate difference of energies such as ionization potential, electron affinity and excitation energy. In spite of the great successes achieved for valence excited spectra, FSMRCC, in the effective Hamiltonian formulation is difficult to be applied for core-excitation spectra, mainly due to intruder state [27-29] induced convergence problem associated with large active space.

As we discussed in chapter 3 and 4, the intermediate Hamiltonian (IH) based FSMRCC (IH-FSMRCC) method [30] is free from intruder state problems and can be used to calculate multiple roots with a large active space in single calculation. The aim of this chapter is to investigate the performance of IH-FSMRCC method for study of core-excitation energy.

This chapter is organized as follows. Section 5.2 contains a brief discussion on the theory of IH-FSMRCC for calculation of core-excitation spectra. Numerical results and discussion are presented in section 5.3. Section 5.4 contains the concluding remarks.

5.2 Theoretical background

We have already discussed the theoretical aspect of IHFSMRCC in detail in chapter 3, but for the sake of completeness, we have discussed the basis idea and working equations of IHFSMRCC method again. As mentioned in chapter 3, $H_{N,eff}$ is defined in the space (model space) with dimension (say, m) much smaller than the actual Hamiltonian, its diagonalization provides desired eigenvalues. When model space configurations (P_M) are not energetically well separated from those of complementary space (Q_M), the method faces convergence problem, termed as intruder state problem. The basic idea of IH formulation is to divide the configuration space into three subspaces namely main, intermediate and outer space with the projection operators P_M, P_I and Q_o respectively. The intermediate space is imposed as a buffer between main and outer space. This intermediate space can be defined formally in terms of excitation level of highest sector cluster operators which defines the FSMRCC equations. The main space of IH formulation is same as the model space of effective Hamiltonian (EH) theory, while the intermediate space (P_I) has been obtained from the complementary space (Q_M) of EH theory by further dividing it into two parts: the intermediate and the outer space. Diagonalization of intermediate Hamiltonian provides the eigenvalues from which only a subset of roots, corresponding to main space, are equivalent to those obtained through effective Hamiltonian theory. In this formulation the final working eq. of FSMRCC can be rewritten as,

$$P_I(\overline{H}_N\{e^S\} - \{e^S\}H_{N,eff})P_M = 0 \tag{5.1}$$

$$H_{N,eff} = P_M \overline{H}_N\{e^S\}P_M \tag{5.2}$$

Defining the operators X as,

$$X = \{e^S - 1\}P_M \tag{5.3}$$

X is defined in such a way that it satisfies,

$$X = Q_M X P_M, \quad X^2 = 0 \tag{5.4}$$

Eqs. (5.1) and (5.2) can be written in terms of X as,

$$P_I(1-X)\overline{H}_N(1+X)P_M = 0 \tag{5.5}$$

$$P_M(1-X)\overline{H}_N(1+X)P_M = H_{N,eff} \tag{5.6}$$

Eqs. (5.5) and (5.6) describe a two step procedure. The first is to solve the quadratic Eq. of X and the second one is to diagonalize $H_{N,eff}$ to obtain the m number of roots, where m is the dimension of the main space. If Eq. (5.5) is satisfied, the same m number of eigenvalues can be obtained by diagonalization of the operator $(1-X)\overline{H}_N(1+X)$ within the $P_o = P_M + P_I$ space. We can replace this two step method with a single step of matrix diagonalization in the following manner. Let us divide the operator X into Y and Z as,

$$X=Y+Z \tag{5.7}$$

$$Y = Q_o X P_M, \quad Z = P_I X P_M \tag{5.8}$$

And $Q_M = P_I + Q_O$ (5.9)

Using the properties of Y and Z, the operator $(1-X)\overline{H}_N(1+X)$ can be written as,

$$(1-X)\overline{H}_N(1+X) = (1-Z)(1-Y)\overline{H}_N(1+Y)(1+Z) \tag{5.10}$$

It is clear from the definition of X (also for Y and Z),

$$(1-X) = (1+X)^{-1} \tag{5.11}$$

From the above interpretation it is clear that if Eq. (5.5) is satisfied, the m number of roots can be extracted equivalently via diagonalization of $(1-X)\overline{H}_N(1+X)$ or

$(1-Y)\overline{H}_N(1+Y)$ operator within $P_O - P_O$ space, as both the operators are related to each other through similarity transformation with respect to an operator (1+Z). Finally we define the Intermediate Hamiltonian as,

$$H_I = P_O(1-Y)\overline{H}_N(1+Y)P_O \qquad (5.12)$$

Using the fact that P_M, P_I and Q_o are the projection operators of the mutually orthogonal space,

Eq. (5.12) can be finally written as,

$$H_I = P_O\overline{H}_N(1+Y)P_O = P_O\overline{H}_N P_O + P_O\overline{H}_N Y P_M \qquad (5.13)$$

For solving the above Eq. we assume that the equations for (0, 0) sector, which is essentially the same as standard SRCC equation, has already been solved. For (0, 1) and (1, 0) sectors,

$$Y^{(0,1)} = Y^{(1,0)} = 0 \qquad (5.14)$$

$$X^{(0,1)} = Z^{(0,1)} = S^{(0,1)} \qquad (5.15)$$

$$X^{(1,0)} = Z^{(1,0)} = S^{(1,0)} \qquad (5.16)$$

For (0, 1) sector (similarly for (1, 0) sector also), the Intermediate Hamiltonian can be written as,

$$H_I^{(0,1)} = P_O^{(0,1)}\overline{H}_N P_O^{(0,1)} \qquad (5.17)$$

Hence for solving the eigenvalue problem for (0, 1) and (1, 0) sectors, $\overline{H}_N$ has to be diagonalized within the space spanned by 1h, 2h1p (one hole and two holes and one particle) and 1p, 2p1h (one particle and two particles and one hole) determinants respectively. Hence it is very transparent to see in IHFSCC framework that eigenvalues of one valence sectors are independent of the choice of model space and the method becomes identical to the IP/EA-EOMCCSD

[50, 51] method. However, for solving the (1, 1) sector (or alternatively (0, 2) and (2, 0) sectors also), cluster amplitudes for (0, 1) and (1, 0) sectors are required explicitly, and it becomes essential to define the model space by choosing some of the valence holes/particles as active. The cluster amplitudes for one valence sectors can be obtained by imposing the intermediate normalization condition on the set of selectively chosen eigenvectors corresponding to the active holes/particles. The matrix formed through column wise arrangement of these eigenvectors can be divided into two sub-matrices. The first one is V_O, obtained from the model space coefficients and the second one is V, obtained from the rest of the matrix. Hence the cluster amplitudes for (0, 1) sector (similarly for (1, 0) sector also) can be obtained as [30, 40]

$$Z^{(0,1)} = [VV_O^{-1}]^{(0,1)} = P_I^{(0,1)} S^{(0,1)} P_M^{(0,1)}$$ (5.18)

Intermediate Hamiltonian matrix for (1, 1) sector is given by,

$$H_I^{(1,1)} = P_O^{(1,1)} \overline{H_N} P_O^{(1,1)} + P_O^{(1,1)} \overline{H_N} Y^{(1,1)} P_M^{(1,1)}$$ (5.19)

Where X, Y and Z operators for (1, 1) sectors are defined as,

$$X^{(1,1)} = Y^{(1,1)} + Z^{(1,1)}$$ (5.20)

$$Y^{(1,1)} = Q_O^{(1,1)} \{S_2^{(0,1)} + S_2^{(1,0)} + S_1^{(0,1)} S_2^{(1,0)} + S_1^{(1,0)} S_2^{(0,1)} + S_2^{(0,1)} S_2^{(1,0)}\} P_M^{(1,1)}$$ (5.21)

$$Z^{(1,1)} = P_I^{(1,1)} \{S_1^{(0,1)} + S_1^{(1,0)} + S_1^{(0,1)} S_1^{(1,0)} + S_2^{(1,1)}\} P_M^{(1,1)}$$ (5.22)

It is clear from the eq. (5.19) that intermediate Hamiltonian for (1, 1) sector can be constructed by the matrix representation of $\overline{H}_N$ within the 1h1p (one hole and one particle determinants) space, modified by the term containing $Y^{(1,1)}$. As $Y^{(1,1)}$ does not contain the $S^{(1,1)}$ amplitudes, the IH matrix for (1, 1) sector can be constructed from the knowledge of cluster amplitudes of lower sectors. Hence, we can conclude that the cluster determining equation for the highest sector (1, 1) is

decoupled from the eigenvalue problem within IH framework. However, the $S^{(1,1)}$ amplitudes can also be determined, if precisely required. Analogous to the case of one valence sectors, this again can be obtained by imposing the intermediate normalization condition on the selectively chosen eigenvectors as,

$$Z^{(1,1)} = [VV_O^{-1}]^{(1,1)} \tag{5.23}$$

It is important here to mention that both connected as well disconnected diagrams appears in Eq. (5.19), as there is no explicit cancellation of disconnected terms. However, this cancellation occurs implicitly during the process of diagonalization. Hence linked cluster theorem holds in this manner. As long as the original (effective Hamiltonian based) FSMRCC Eqs. is given by Eqs. (5.1) and (5.2), its reformulation through intermediate Hamiltonian technique (given by Eq. 5.19), is straightforward. This is usually the case of CMS and some of the special IMS (like (1, 1) sector), where $H_{N,eff}$ is explicitly expressible in terms of Ω. This strategy has been used very recently by Musial et al to extend the IH formulation and its implementation for (0, 2) and (2, 0) sectors [38, 39]. In this IH formulation of FSMRCC theory, equations don't have to be solved in coupled iterative manner. Rather, the eigenvalues are obtained through direct diagonalization procedure. This helps one to safely reach the convergence with larger model space, which significantly improves the correlation effects in many cases. Also as the final diagonalization occurs in 1h1p space, this allows one to perform the calculation with significantly larger basis set. In the next section we present some numerical results of core excitation energy of few molecules through FSMRCC method in IH framework.

5.3 Computational details, results and discussions:

The computational procedure for getting core excitation energy through IHFSMRCC involves the following steps. We have solved the ground state CCSD equations and obtained T amplitudes after solving restricted Hartree-Fock equation. For the efficient computational implementation, one and two body parts of $\bar{H}_N$ are constructed with the help of T and stored in the disk while three body part of $\bar{H}_N$ is being constructed instantly, whenever required. These $\bar{H}_N$ intermediates are used to solve the IH matrix eigenvalue problem for (0, 1) and (1, 0) sectors. As the dimension of IH matrix for (0, 1) and (1, 0) sectors is very large, an efficient diagonalization routine has to be used for solving the eigenvalue problems for a few of the selected roots. In practice, this is followed by Nakatsuji-Hirao algorithm [52] of non symmetric matrices, which is the generalization of Davidson's algorithm [53] for symmetric matrices. Once the eigenvalue problem is solved, eigenvectors for selective roots are transformed into $S^{(0,1)}$ and $S^{(1,0)}$. These S amplitudes are used to construct the IH matrix for (1, 1) sector and solve the eigenvalue problem.

We have performed our core excitation energy calculation for three test systems: N_2, H_2O and CH_4. For each system, we have calculated the excitation energies in at least two basis sets. The core excitation energy for all three molecules, have been reported in cc-pVDZ and cc-pVTZ basis. In addition to this, cc-pCVTZ basis has also been used for CH_4 molecule. The geometries for each molecule have been given with their tables. We have taken EOMCC excitation energies and corresponding experimental values from reference 49 and 54 for comparison. Due to IH formulation of FSMRCC method, we were able to enlarge our active space up to a significant extent. It is important to mention that in IHFSMRCC method with singles and doubles (SD), final diagonalization occurs in 1h1p space while in EE-EOMCCSD method the same occurrs in the 1h1p and 2h2p space. Both the methods using generalized Davidson algorithm for final matrix diagonalization,

have the scaling of N^6 but due to presence of two active lines (one active hole line and one active particle line) in N^6 scaling diagrams of IHFSMRCCSD method, its computational cost is reduced in compare to EE-EOMCCSD. The computational cost in each iteration of the generalized Davidson algorithm is further reduced due to fact that as compare to EE-EOMCCSD, in IHFSMRCCSD, lesser number of terms has to be coded using diagrammatic technique. The practical problem with EE-EOMCCSD method is that it is extremely difficult to converge for the roots dominating with single core excitations. Even if it converges, it takes huge number of iterations to achieve this. It is important to mention that one has to face the similar kind of difficulties in IHFSMRCCSD method also when we use larger active space and follow the Davidson algorithm for root convergence. However, this problem is being compensated because one can afford huge number of iterations in IHFSMRCCSD method, as the computational cost in each iteration has already been reduced. In addition, due to reduced dimension of diagonalization space one can afford the complete matrix diagonalization to obtain all the roots simultaneously instead of following the iterative Davidson procedure for a particular root. However, in complete diagonalization procedure one has to be careful in mapping the eigen values with their electronic transition as, due to non-Hermitian nature of the matrix, its eigenvectors may have complex component and may mislead to wrong transition.

We have denoted the number of active occupied and virtual orbitals as nacth and nactp respectively in our data tables. It is very clear from the tables 5.1, 5.2 and 5.3, that the IHFSMRCC values are closer to experimental results than that of EOMCC values consistently. Both the IHFSMRCC and EOMCC core excitation energy values are decreased with increasing the basis sets. As the basis are increased, IHFSMRCC values are systematically improved towards the experimental values.

Table 5.1 Adiabatic core excitation energies for N$_2$ ($1\Sigma_g \rightarrow 1\Pi_g$)

Basis	EOM-CCSD [54]	IH-FS-MRCCSD (nacth, nactp)	Experimental [49]
cc-pVDZ	404.43	404.15 (7, 10)	400 eV (with the 1.8–2.0 eV resolution)
cc-pVTZ	401.68	401.34 (7, 18)	

Note: Geometry: R (N–N) = 2.068 a.u.
Energies are in e.V.

Table 5.2 Adiabatic core excitation energy of H$_2$O (1a$_1$-4a$_1$)

Basis	EOM-CCSD [54]	IH-FS-MRCCSD (nacth, nactp)	Experimental [49]
cc-pVDZ	538.40	537.83 (5,10)	534.0
cc-pVTZ	535.34	534.58 (5,20)	

Note: Geometry: R (O–H) = 0.9772A° H-O-H = 104.52°.
Energies are in e.V.

Table 5.3 Diabatic core excitation energies for CH$_4$ [C 1s →LUMO(A$_1$)]

Basis	EOM-CCSD	IH-FS-MRCCSD (nacth, nactp)	Experimental [55]
cc-pCVTZ	XXX	287.79 (5, 20)	
cc-pVDZ	290.84	290.26 (5, 10)	287.99
cc-pVTZ	XXX	288.10 (5, 15)	

Note: Geometry of G.S. R (C–H) = 1.087A°
Geometry of Excited State R (C–H) = 1.032A°
Energies are in e.V.
XXX: Did not converge

5.4 Concluding remarks:

Effective Hamiltonian based FSMRCC theory suffers from intruder state problem when the model space is enlarged in order to target more number of states and specially the excited states dominated with excitation of single core electron. Its reformulation through IH technique provides a numerically stable and cost effective way to obtain the roots via direct diagonalization procedure. Reformulation of FSMRCC method through IH technique opens a path for evaluation of excited state properties with larger model space. This not only significantly improves the correlation effects but also enables one to access the excitation energy for core electrons. In IH-FSMRCC excitation energy calculation, final diagonalization takes place in 1h1p space. This allows one to perform the calculations for excitation energy as well as excited state properties using bigger basis sets. In IH formulation of FSMRCC, cluster amplitudes for highest sector (in this case (1, 1) sector) are decoupled from the eigenvalue problem. This helps one to reach the computational efficiency. Our preliminary test results show that the IHFSMRCCSD method with large active space performs slightly better than the well established EE-EOMCCSD method, but the extensive applications and detailed analysis about the effect of basis set and active space is essential in order to draw some discrete conclusion. Research work along these lines is in progress and would be reported in our future publication.

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