

**LINEAR RESPONSE APPROACH TO FOCK-SPACE
MULTI-REFERENCE COUPLED CLUSTER**

Thesis submitted to the
University of Pune
for the Degree of

Doctor of Philosophy
in **Chemistry**

By

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CERTIFICATE

This is to certify that the work presented in this thesis entitled,

Linear response approach to Fock-space multi-reference coupled cluster

submitted by **Arijit Bag**, for the degree of Doctor of Philosophy, was carried out by the candidate under my supervision in the Physical Chemistry Division, National Chemical Laboratory, Pune 411008, India. Any material that has been obtained from other sources has been duly acknowledged in this thesis.

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DECLARATION

I, **Arijit Bag** declare that the thesis entitled

Linear response approach to Fock-space multi-reference coupled cluster

submitted by me to **University of Pune** for the degree of Doctor of Philosophy is the record of work carried out by me during the period from 7th January, 2004 to 18th May, 2009 under the guidance of Dr. Sourav Pal, Physical Chemistry Division, National Chemical Laboratory, Pune 411008, India and has not formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other institution of Higher learning.

I further declare that the material obtained from other sources has been duly acknowledged in the thesis. I further declare that the work presented in the thesis or any part thereof has not been submitted by me to this or any other University for obtaining any other degree or diploma.

Date:

Place:

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List of Publications

1. “Analytical Dipole Moments and Dipole Polarizabilities of Oxygen Mono-Fluoride and Nitrogen Dioxide: A Constrained Variational Response to Fock-Space Multi-Reference Coupled-Cluster Method”
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3. “On some aspects of Fock-space multi-reference coupled-cluster singles and doubles energies and optical properties”
-**A. Bag**, P.U.Manohar, K. R. Shamasundar, N. Vaval, S. Pal;
(in press)
4. “Static hyper-polarizability of open shell molecules computed at the FSMRCCSD level using constrained variational approach”
-**A. Bag**, S. Bhattacharya, S. Pal;
(in press)
5. “Excited state static hyper-polarizability of closed shell molecules using CVA-FSMRCC : Theory and application”
-**A. Bag**, S. Pal;
to be communicated

Abstract

Multi-reference coupled-cluster (MRCC) [1–6] method emerged as an efficient tool to describe the electronic structure of degenerate and quasi-degenerate systems. Development of linear response in MRCC framework using Lagrange variational technique is the choice of interest for the calculation of molecular properties at the ground state as well as at the electronic excited states. There are two subclasses of MRCC methods, which have been studied extensively. One is the multi-root description via an effective Hamiltonian approach [7, 8] and the other describes a specific root, known as the state-specific MRCC approach [9]. In multi-root effective Hamiltonian approaches, exact energies of the corresponding strongly interacting near-degenerate states are obtained as roots of the effective Hamiltonian via diagonalization. This class of methods is further subdivided into Hilbert space and Fock space approaches depending on the way the dynamical part of electron correlation is described [1–7, 10–14]. In the Hilbert space approach a state universal wave operator which contains different cluster operators for each of the determinants in the model space [1, 5, 6], is used. This method has been used for studying PES, bond-dissociation, etc. However for PES, the state selective MRCC method developed by Mukherjee and co-workers [9] has been found more suitable from the point of view of circumventing the important problems of intruder states. The Fock-space (FS) MRCC [1–5, 10–14], in general, is found to be suitable for cases like ionization, electron-attachment and electronic excitation of molecules and is based on the concept of a common-vacuum and a valence universal wave-operator. The effective FS Hamiltonian scheme of Meissner [8] eliminates intruder states in a computationally practical way. The model space is composed of configurations obtained by combinations of electron occupancies among what are called active orbitals. The occupancies of the active orbitals are

denoted in terms of number of the active particles and active holes with respect to the vacuum.

Obtaining energy derivative in the context of MRCC methods was challenged due to the multi-root nature of the effective Hamiltonian. A response from any of the roots span the space, perturbation of all roots simultaneously would proliferate the excited states. Along the lines of SRCC, the analytic linear response method based on Monkhorst's approach [15] was initiated by Pal [16] long ago. The computational developments and implementation of the method were done later by Ajitha *et al* [17–19] for obtaining dipole moments of doublet radicals and low-lying excited states of molecules. However, the approach was quite unsatisfactory, since it required expensive evaluation of cluster amplitudes derivatives for every mode of perturbation.

In the SRCC context, this problem was solved by incorporation of Z-vector technique [20] or equivalently, the constrained variational approach (CVA) [21], which was based on the method of Lagrange undetermined multipliers. Pal and co-workers obtained FSMRCC energy derivatives similarly by using a Lagrange functional for both Fock and Hilbert space [22, 23]. This was also pursued by Szalay [24] independently. However, while the formulation of Szalay was applicable for complete model spaces (CMS) only, that by Pal and co-workers is applicable for a general incomplete model space (IMS) cases and simplifies to Szalay's formulation in the case of CMS. Advantage of this approach is that, it is a variational method and obey $(2n+1)$ rule. Thus, it is possible to obtain higher order energy derivatives with the knowledge of lower order cluster amplitude derivatives and a set of perturbation independent vectors, the Lagrange multipliers. It can be easily shown that the equations of cluster amplitudes are completely decoupled from those of the Lagrange multipliers. There is a partial decoupling amongst the cluster amplitudes, i.e. the lower valence cluster amplitudes are decoupled from the higher valence ones. This is commonly referred to as subsystem embedding condition (SEC).

The Λ -equations, on the other hand, contain the T amplitudes, which are known. The FS Λ -equations are also partially decoupled, but in a reverse SEC manner.

The implementation of the above approach in FSMRCC framework were recently done by Manohar et. al. [25, 26] using singles and doubles (SD) truncation of the wave operator. This thesis focuses on development of CVA based FSMRCC method for excited states and doublet radicals and implementation of these for evaluation of dipole moment, polarizability and first hyper-polarizability of ionized, electron attached and electronically excited states of molecules. The calculations have been presented up to one-hole one-particle Fock space sector with respect to the restricted Hartree-Fock of the ground state of the molecules as vacuum. The one-valence defined with the closed shell cation or anion problems can describe the doublet open-shell system.

As we know, excited state properties are required for the understanding of reaction kinetics, spectroscopy and others, CVA-FSMRCC method is implemented for the electronic excited states. The theory is developed by Pal and Shamasundar but the implementation was initiated by Pal and Manohar, which is extended through the work presented here. For the first electronic excited state, due to the spin integration, there are two types of cluster amplitudes as well as Lagrange multipliers which are termed as direct and exchange. For the triplet excited state only the direct terms are required while for the singlet excited state both direct and exchange terms are required. In that sense, it may be concluded that the triplet is decoupled from the singlet. Thus, the amplitudes of the direct types and of course, the triplet excited state properties, are evaluated first and then using these values, amplitudes of the exchange types and the singlet excited state properties have been calculated.

In chapter 1, a general introduction has been given for both single-reference and

multi-reference methods. Linear response formalism for both single-reference and multi-reference coupled-cluster methods are described. Partial decoupling of the cluster amplitudes are exploited. Z-vector technique and Lagrange formulation for SRCC as well as MRCC are presented in this chapter.

In chapter 2, CVA-FSMRCCSD theory and the Lagrange formulation have been discussed for open shell doublet molecules and the expressions for first- and second-order energy derivatives are given. Also analytic dipole moments and dipole polarizabilities of Oxygen mono-fluoride and Nitrogen dioxide using CVA-FSMRCCSD method are presented.

Chapter 3 includes CVA-FSMRCCSD method for calculation of excited state properties of closed shell molecules. Theoretical details have been given with description of code developed. Application of this method for calculation of dipole moment and polarizability of low-lying excited states of Water, Ozone, Carbon mono-hydride cation and Hydrogen mono-fluoride are presented.

First static hyper-polarizabilities of few doublet radicals are presented in chapter 4. The implementation and the code development for this purpose has been described. Static hyper-polarizabilities of OH, OF, NO and NO₂, at the ground state is presented. Orbital-relaxed finite field FSMRCC values have been reported for comparison.

In chapter 5, static hyper-polarizabilities of the first electronic excited states of closed shell molecules are presented. Calculations were done using CVA-FSMRCCSD method. The implementation and the code developed for this purpose has been discussed. The singlet and the triplet excited states hyper-polarizabilities of water, ozone and carbon mono-hydride cation are presented.

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Chapter 1

Molecular response properties and many-body problem in quantum mechanics : A brief overview

In this chapter, recent developments in quantum chemistry and linear response technique are discussed. Starting from Hartree-Fock, Configuration Interaction, Møller-Plesset Perturbation theory and coupled-cluster methods are described based on single reference model space. Subsequently, multi-reference versions of these methods are presented. Both Fock-space and Hilbert-space multi-reference coupled-cluster methods are discussed. Linear response technique for single-reference and multi-reference coupled-cluster methods, suitable for the work presented in this thesis, are also described.

1.1 Introduction

Over the last few decades, there has been significant progress in the study of electrical response properties of molecules. A number of reviews highlight the diverse theoretical, conceptual and computational thrusts that have led to such progress [1–6]. The nature of electrical response as molecules approach and interact with applied electric field, has been studied to finer and finer levels of detail and this has been done for problems that now range from small molecules to clusters and polymers including solvent effects. Electrical response is required for interpreting and accounting for certain intermolecular behaviors. The motivation and the utility of working with electrical response is that it involves well-defined properties that are intrinsic to molecules, e.g dipole moment, polarizability, hyper-polarizability etc. It is also important for understanding of chemical and physical phenomenon. Another important motivation is that the electrical response serves as a bridge between classical and quantum mechanical interaction analysis. Careful treatment of electrical response is required because, it often seems to be the dominant source of changes in properties that are of enough interest to be sought spectroscopically, e.g. nuclear quadrupole coupling [7], chemical shielding [8, 9] and electrical properties themselves [10].

Depending on the aim of the study, quantum chemistry can be further subdivided into two branches, namely, molecular structure [11] and molecular dynamics [12]. Molecular dynamics depends upon the success of molecular structure theory. Therefore, it is very important to develop efficient method to study the molecular structure accurately. Hartree-Fock (HF) [11, 13–15] method is the simplest electronic structure method. However, due to the lack of dynamical electron correlation, Hartree-Fock method is unable to fulfill the requirements of theoretical chemists. There are several many-body methods which are fully correlated, e.g., configuration interaction (CI)

[11, 16, 17], many-body perturbation theory (MBPT) [18–23] and coupled-cluster (CC) [24–27] methods. Full CI is considered as exact, but computationally expensive and truncated CI is not size-extensive and size-consistent. MBPT is also a very powerful method and often yields reasonably good results at low order of perturbation. On the other hand, CC methods have caught special attraction because of size-extensivity and accurate treatment of electron-correlation effects, and have thus become a promising tool for molecular structure studies. Recent development of analytical response [28, 29] of these methods has opened up an efficient technique for obtaining energy derivatives, gradients, Hessians etc.

However, for degenerate and quasi-degenerate states, single reference description is not sufficient. Non-dynamical electron correlation, in general, is taken care through the formation of multi-determinant model space and hence, they are commonly known as multi-reference (MR) theory. Analogous to SR methods, this includes MRCI [30], MRMP [31–34], MRCC [35–37] etc. In these methods, the dynamical electron correlation is incorporated in the similar way as the corresponding SR methods.

There are two subclasses of MRCC methods, which have been studied extensively. One is the multi-root description via an effective Hamiltonian approach [38, 39] and the other describes a specific root, known as the state-specific MRCC approach [40]. In multi-root effective Hamiltonian approaches, exact energies of the corresponding strongly interacting near-degenerate states are obtained as roots of the effective Hamiltonian via diagonalization. This class of methods are further subdivided into Hilbert space and Fock space approaches depending on the way the dynamical part of electron correlation is described [36, 38, 41–52]. In the Hilbert space approach, a state universal wave operator which contains different cluster operators for each of the determinants in the model space [36, 43, 44], is used. This method has been used for studying potential energy surface (PES) and bond-dissociation. However, for PES, the state selective MRCC

method developed by Mukherjee and co-workers [40] has been found to be more suitable from the point of view of circumventing the important problems of intruder states. The Fock-space (FS) MRCC [36, 41–43, 45–52], in general, is suitable for cases like ionization, electron-attachment and electronic excitation of molecules and is based on the concept of a common vacuum and a valence-universal wave-operator. The effective FS Hamiltonian scheme of Meissner [39] eliminates intruder states in a computationally practical way. The model space is composed of configurations obtained by combinations of electron occupancies among what are called active orbitals. The occupancies of the active orbitals are denoted in terms of number of the active particles and active holes with respect to the vacuum.

Parallel to this, methods like equation-of-motion (EOM) CC, coupled cluster linear response (CC-LR) [53, 54], symmetry-adapted cluster configuration interaction (SAC-CI) [55, 56], etc. have also been developed to handle certain classes of quasi-degeneracy. EOM-CC method has been developed extensively for excited, ionized and electron attached states [57–73]. For one valence problem in Fock space i.e. for ionization potential and electron affinity calculation, EOM-CC and FSMRCC are equivalent. However, for excitation energy calculation, such equivalency disappears. It was shown by Bartlett [68] that while only linked diagrams remain in FSMRCC, the same is not true for EOM-CC, though this only affects charge transfer separability. However, recently developed similarity transformed (ST) EOM-CC method of Nooijen and co-workers [69, 70] is size-extensive. CC-LR method developed by Jørgensen's group [53, 54] has also been used extensively for the calculation of excitation energies. The excitation energies obtained by CC-LR are identical to the EOM-CC excitation energies and thus, CC-LR has the same failing for charge transfer separability.

EOM-CC derivatives for property calculation was initiated and implemented by Stanton [71] first and then by Stanton and Gauss [61, 72]. Gradients using STEOM-CC was

implemented by Nooijen and coworkers [73] using a Lagrange undetermined multiplier, which is similar to the method followed in the present work.

However, obtaining energy derivatives in the context of multi-root MRCC methods was a challenge. Since a response from any of the roots span the space, perturbation of all roots simultaneously would proliferate the excited states. Along the lines of SRCC, the analytic linear response method based on Monkhorst's approach [28] was initiated by Pal [74] long ago. The computational developments and implementation of the method were done later by Ajitha *et al* [75–77] for obtaining dipole moments of doublet radicals and low-lying excited states of molecules. This approach was quite unsatisfactory, since it requires expensive evaluation of cluster amplitudes derivatives for every mode of perturbation.

In SRCC context, this problem was solved by incorporation of the Z-vector technique [78] or equivalently, the constrained variational approach (CVA) [79], which was based on the method of Lagrange undetermined multipliers. Pal and co-workers obtained FSMRCC energy derivatives by using a Lagrange functional for both Fock and Hilbert space [80, 81]. This was also pursued by Szalay [82] independently. However, while the formulation of Szalay was applicable for complete model spaces (CMS) only, that by Pal and co-workers is applicable for a general incomplete model space (IMS) cases and simplifies to Szalay's formulation in the case of CMS. This single root method provides a cost-effective tool to obtain higher order energy derivatives with the knowledge of lower order cluster amplitude derivatives and a set of perturbation independent vectors, the Lagrange multipliers.

The computational developments of the above approach in FSMRCC framework were recently done by Manohar *et. al.* [50, 83] using singles and doubles (SD) truncation of the wave operator and the method was then implemented for analytic dipole moments and polarizabilities of doublet radicals [50, 51].

In this thesis, above mentioned method is implemented for the calculation of dipole moment, static dipole polarizability and static hyper-polarizability of open shell molecules and radicals. The same is also done for the low-lying excited states of closed shell molecules. In this chapter, some earlier developments of many-body methods, multi-reference methods and linear response techniques are discussed. Implementation of CVA-FSMRCCSD method is discussed in the remaining chapters.

1.2 Context of molecular structure theory

In quantum mechanics, hydrogen atom (H) is exactly solvable problem as there is only one electron and one proton. Hydrogen like atoms e.g. He^+ , Li^+ etc. are also solvable. Complexity arises due to the coulombic interactions among electrons when number of electrons becomes more than one. In case of a molecules, situation becomes more and more complicated due to the presence of more than one positive center. There are several quantum mechanical bound states with various types of attractive and repulsive forces within the system.

1.2.1 Schrödinger wave equation for molecules

Electronic structure theory of atoms and molecules is based on the time-independent Schrödinger wave equation [11, 84]

$$\hat{H}\Psi = E\Psi \quad (1.1)$$

There is also time dependent Schrödinger wave equation where wave function (Ψ) has time containing part. However, for molecular structure calculations stationary states are more important and hence for most of the cases time independent Schrödinger wave equation is used. In Eq. (1.1), \hat{H} is Hamiltonian operator which is total energy operator of a system and composed of kinetic energy term, potential energy term and energy due to

interaction of the system with its surroundings. The interaction with surrounding is often related to electric and/or magnetic properties of the system. In the absence of external field, only kinetic energy and potential energy terms contribute to the Hamiltonian. The Hamiltonian for a system of M nuclei and N electrons can be written as [11]

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

where,

$$\begin{aligned} \hat{T}_n &= - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2; & \hat{T}_e &= - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 \\ \hat{V}_{nn} &= + \sum_{A=2}^M \sum_{B=1}^{A-1} \frac{Z_A Z_B}{\|\vec{R}_A - \vec{R}_B\|}; \\ \hat{V}_{ne} &= - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A}{\|\vec{r}_i - \vec{R}_A\|} \quad \text{and} \quad \hat{V}_{ee} = + \sum_{i < j}^N \frac{1}{\|\vec{r}_i - \vec{r}_j\|} \end{aligned} \quad (1.3)$$

In the above equation, \hat{T}_n is the sum of kinetic energies of nuclei, \hat{T}_e is the sum of kinetic energies of electrons, \hat{V}_{nn} , \hat{V}_{ne} and \hat{V}_{ee} are the sum of the potential energies due to nuclear-nuclear repulsions, nuclear-electron attractions and electron-electron repulsions respectively. \vec{R}_A and \vec{r}_i are spatial coordinates of A -th nucleus and i -th electron respectively.

For N -electron system, Schrödinger wave function is a complicated function of spatial coordinates of nuclei and space-spin coordinates of electrons. Space-spin coordinate of i -th electron is considered as $\vec{x}_i = \{\vec{r}_i, \xi_i(\sigma)\}$ where $\xi_i(\sigma)$ is spin of i -th electron. Thus, wavefunction of N -electron system can be written as $\Psi(\vec{R}_1, \dots, \vec{R}_M, \vec{x}_1, \dots, \vec{x}_N)$. According to Pauli's exclusion principle, there may exist maximum two electrons in a spatial orbital but for space-spin orbital only one electron is possible. As electrons obey Fermi-Dirac statistics the wave function for many electron system must be anti-symmetric with respect to the interchange of space-spin coordinates of any two electrons

and may be written as

$$\Psi(\vec{x}_1, \dots, \vec{x}_i, \dots, \vec{x}_j, \dots, \vec{x}_i, \dots, \vec{x}_N) = -\Psi(\vec{x}_1, \dots, \vec{x}_j, \dots, \vec{x}_i, \dots, \vec{x}_N) \quad (1.4)$$

Anti-symmetry can be brought in by using determinant rather than simple product, which is commonly known as ‘‘Slater determinant’’, expressed as

$$\Phi_0(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_1(\vec{x}_2) & \dots & \chi_1(\vec{x}_N) \\ \chi_2(\vec{x}_1) & \chi_2(\vec{x}_2) & \dots & \chi_2(\vec{x}_N) \\ \vdots & \vdots & & \vdots \\ \chi_N(\vec{x}_1) & \chi_N(\vec{x}_2) & \dots & \chi_N(\vec{x}_N) \end{vmatrix} \quad (1.5)$$

1.2.2 Electronic Hamiltonian in Born-Oppenheimer approximation

It is very difficult to solve eigen value Eq. (1.1), using full Hamiltonian as described in Eq. (1.2) even for small systems. But if we observe Eq. (1.2) carefully, we should see \hat{T}_n and \hat{V}_{nn} depend on nuclear coordinates and \hat{T}_e and \hat{V}_{ee} depend on electronic coordinates while \hat{V}_{ne} depends on both nuclear as well as electronic coordinates. Since, nuclei are much heavier than electrons, while considering electronic motions, they can virtually be assumed to be stationary. Thus we can calculate electronic properties, e.g. electronic energy, wave function etc., for any fixed geometry. This is known as frozen-nuclei Born-Oppenheimer approximation (BOA). As a consequence of this approximation, the kinetic energy of nuclei (\hat{T}_n) drops out and the inter-nuclear repulsion energy (\hat{V}_{nn}) in Eq. (1.2) becomes constant. As addition of any constant to an operator does not affect the eigenfunctions and simply adds to the eigenvalues, the problem reduces to the solution of electronic Hamiltonian which can be written as

$$\begin{aligned} \hat{H}_{ele} &= \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \\ &= -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A}{\|\vec{r}_i - \vec{R}_A\|} + \sum_{i < j}^N \frac{1}{\|\vec{r}_i - \vec{r}_j\|} \end{aligned} \quad (1.6)$$

1.2.3 Basic criteria for a good molecular structure theory

Even after BOA, we need further approximation due to the presence of inter electronic repulsion term (\hat{V}_{ee}). The accuracy of the approximate method can be improved systematically. The method should, at all the stages, satisfy some basic conditions so that it may be considered as a “theoretical model” for electronic structure calculations. These criteria, as were proposed by Pople *et. al.* [86] about forty 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 molecular systems, electronic configurations and symmetry.
2. The method should be invariant with respect to classes of transformation. Unitary transformations should not alter the orbital degeneracy.
3. The method should be **size-consistent**. A method is said to be size-consistent if energy obtained by its implementation on a system of several molecules at non-interacting limit is same as the sum of the energies obtained by separate implementations of the method on these molecules.
4. The method should be **size-extensive** which means energy of a strongly interacting many-electron system for a given potential should be approximately proportional to number of electrons in the system.
5. The method should be computationally cost effective and efficient.

Size-consistency and size-extensivity are most important criteria since, the efficiency and accuracy of theoretical methods are governed by these conditions. We also need good theoretical methods for open-shell system and excited states.

1.3 Hartree-Fock theory

The Hartree-Fock (HF) approximation [11, 13, 14] is central to all attempts to find and describe approximate solution to the electronic part of Schrödinger equation. It is based on the fact that, stationary states of many systems, in particular, ground states of closed shell atoms and molecules, having all paired electrons can be described by single slater determinant (see Eq 1.5).

Electrons are assumed to be independent of each other and spherically averaged inter-electronic repulsion potential is considered. We can approximately vary the spin orbitals constraining them only to the extent that they remain orthogonal i.e. $\langle \chi_a | \chi_b \rangle = \delta_{ab}$, until the energy being minimum. In this way we get the best spin orbitals which minimize the energy. This procedure leads to integro-differential equations referred to as Hartree-Fock equations, which are solved iteratively so as to make $\langle \Phi_0 | \hat{H}_{ele} | \Phi_0 \rangle$ stationary. The Hartree-Fock equation may be stated as given bellow.

$$\hat{f}(\vec{x})\chi_a(\vec{x}) = \epsilon_a\chi_a(\vec{x}) \quad (1.7)$$

$$\hat{f}(\vec{x}) = \hat{T}_e + \hat{V}_{ne} + v_{HF}(\vec{x}) \quad (1.8)$$

$$v_{hf}(\vec{x}) = \sum_{j=1}^N J_j(\vec{x}) + \sum_{j=1}^N K_j(\vec{x}) \quad (1.9)$$

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

$$K_j(\vec{x})\chi_i(\vec{x}) = \int dx' \frac{\chi_j^*(\vec{x}')\chi_i(\vec{x}')}{|\vec{x} - \vec{x}'|} \chi_j(\vec{x}) \quad (1.11)$$

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

of the wavefunction.

Hartree-Fock method is very good for atoms as equations are exactly solvable. However, for molecules the explicit integration of the two-electron interaction terms is difficult as the orbitals involved are centered at different nuclei. This was overcome by Roothan [15] who introduced the idea of basis set expansion. For closed-shell systems 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. One may explicitly solve the HF equations using spin-orbitals which is called unrestricted HF (UHF). While an RHF or ROHF determinant is a pure eigenfunction of total spin operator, UHF determinant, in general, is not.

In HF theory electron-electron repulsion is taken as an average way. Yet it recovers almost 99% of the total energy. The difference between exact energy and HF energy is called correlation energy.

1.4 Post Hartree-Fock methods

HF theory deals the best single-determinant form of the exact wavefunction and predicts the energy of the system very accurately. However, most of the chemical phenomena like binding energy, excitation energy, activation energy, etc. require the energy differences rather than absolute energy of a specific state. Unfortunately the variation principle does not hold for energy differences. Thus for chemist point of view we need further improvement to go beyond the HF approximation and treat the electron correlation effects correctly.

Meaning of electron correlation

Electron correlation arises due to the fact that HF method is an effective one particle method and hence, it can not account instantaneous electron-electron repulsion between anti parallel spin. Electron correlation between anti-parallel spin is known as dynamical electron correlation. Correlation energy is defined as the energy difference between exact energy and Hartree-Fock energy.

$$E_{corr} = E_{ex} - E_{HF} \quad (1.12)$$

Since HF is the upper bound to the exact energy, correlation energy, in general, is negative.

1.4.1 Configuration interaction method

Configuration interaction (CI) [11, 16, 17] is conceptually the simplest and traditional method to recover correlation energies. HF theory provides with a set of orthonormal orbitals as eigenfunctions of the Fock operator which is exploited in the wavefunction expansion. For an N -electron system, a complete set of anti-symmetric N -electron functions can be obtained by all possible combinations of these orbitals. One of these configuration will of course, be the HF configuration. The exact wavefunction of the system includes all possible configurations.

The method looks quite simple, but, in practice, it is not. The most fundamental problem lies in impossibility of including the complete set of orbitals. Hence, for practical purpose, a finite set of orbitals is considered in the form of basis set. The number of basis functions can be chosen according to the accuracy requirements. The use of finite basis set consequently limits the number of configurations. For example, if X -orbital basis set is used to describe an N -electron system, there will be ${}^X C_N$ possible configurations. If all these configurations are included in the wavefunction, it is called Full CI

(FCI) wavefunction and is exact in the basis set limit. The coefficients of the configurations can be variationally optimized to minimize the total energy of the system. The coefficients and the respective configurations can be labeled in various ways. The most convenient and commonly used scheme is to define the configurations as excitations of electrons with respect to HF occupancies. Thus the configurations can be singly excited, doubly excited and so on, up to N -tuply excited with respect to HF configuration. The wavefunction can thus be represented as

$$\Psi = \Phi_0 + \sum_{i \in occ} \sum_{a \in virt} C_i^a \Phi_i^a + \sum_{i,j \in occ} \sum_{a,b \in virt} C_{ij}^{ab} \Phi_{ij}^{ab} + \dots \quad (1.13)$$

Intermediate normalization has been used in the above expansion, although, some other normalization schemes can as well be used. The Φ_i^a indicates a singly excited determinant formed by excitation of electron from i -th orbital (occupied) in HF determinant to the a -th (virtual) orbital. Similarly, Φ_{ij}^{ab} indicates doubly excited determinant obtained by exciting the electrons from i -th and j -th orbitals to a -th and b -th orbitals respectively. The corresponding coefficients are obtained using linear variation method. This leads to eigenvalue problem for the Hamiltonian matrix. The matrix elements are calculated using Slater-Condon rules [11]. The lowest eigenvalue and the eigenvectors corresponds to the ground state of the system. CI coefficients can be obtained by method of projection. However, since the expression is linear in coefficients, it can be shown that the method is equivalent to the linear variation method. Recently, far more advanced approaches are being used for solution of the CI equation. Notable amongst them are use of configuration state functions (CSF) [16, 17], Davidson iterative diagonalisation [90], direct CI [91], etc. The CSF is based on use of spin-adapted N electron functions. Depending on the way, the CSF are obtained there have been two approaches, namely, unitary group approach (UGA) [92, 93] and symmetric group approach (SGA) [93, 94].

FCI fulfills all the criteria for a theoretical model. But, the dimension of the

wavefunction increases rapidly with the number of electrons as well as basis functions. It becomes practically impossible to use FCI even for small molecules with moderate size basis sets. Use of smaller basis set also affects the accuracy. Thus, FCI is computationally unattractive and one has to truncate the expansion of the excited determinants. Due to Brillouin's theorem, the singly excited configurations alone cannot improve the ground state energy. One must include the doubly excited configurations to improve the ground state energy. The expansion of the wavefunction formed by excluding all the configurations except HF and doubly excited configurations is known as CI doubles (CID) and recovers most of the correlation energy. Inclusion of singly excited determinants in addition to the doubly excited determinants is called CI singles and doubles (CISD). Although singly excited determinants do not directly mix with Hartree-Fock, they interact through the doubly excited determinants and further improve the correlation energy. More accuracy can be established by including the higher excited configurations.

While the truncations to CI expansion make it cost-effective, they sabotage the size-consistency and size-extensivity of the wavefunction. As defined earlier, size-consistency refers to additive separability of the energy during fragmentation. For example, if a molecule AB dissociates into its fragments A and B then the method is size-consistent if the following condition is fulfilled.

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

The additive separability of energy demands that $\Psi_{AB} = \Psi_A\Psi_B$. If the wavefunctions are obtained by CISD method, the Ψ_{AB} would include upto two-electron excitations, whereas, the product $\Psi_A\Psi_B$ would include upto four-electron excitations indicating that the condition $\Psi_{AB} = \Psi_A\Psi_B$ cannot be true and thereby invalidating the additive separability of the energy. Thus it can be seen that, CISD or more correctly, any truncated CI will lack the feature of size-consistency. Size-extensivity is related to

scaling of the energy of the system with number of electrons. Due to non-interacting picture, HF energy properly scales with the number of electrons. Hence, size-extensivity is considered as a requirement of correlated methods. If total energy (and hence, the correlation energy) of a system approximately varies linearly with the number of electrons, the method is said to be size-extensive. The energy obtained from truncated CI is found to show sub-linear dependence [11] with the number of electrons misinterpreting zero correlation energy per electron as the number of electrons tends to infinity. Thus, any truncated form of CI cannot be considered as “theoretical model”.

1.4.2 Many body perturbation theory

Many body perturbation theory (MBPT) [18–23] is another useful method to systematically improve electron correlation effects. The Hamiltonian is partitioned into zeroth-order Hamiltonian (\hat{H}_0) and perturbed Hamiltonian (\hat{H}'). The eigenfunctions $\{\Psi_i^0\}$ of \hat{H}_0 form a complete set with the corresponding eigenvalues denoted by E_i^0 . The other, weakly interacting part is unknown. In MBPT context, this is viewed as a perturbation to the zeroth order Hamiltonian and is denoted by V . The matrix elements $\langle \Psi_i^0 | V | \Psi_j^0 \rangle$ are assumed to be known. Depending on the way, the partitioning is done, there are two variants, namely Møller-Plesset (MP) and Epstein Nesbet (EN) perturbation theories. The stationary states $\{\Psi_i\}$ and the eigenvalues E_i of exact Hamiltonian are determined from these known quantities. This is done by introduction of a perturbation parameter λ in the definition of exact Hamiltonian, which is smoothly varied from 0 to 1.

$$\hat{H}^{(\lambda)} = \hat{H}_0 + \lambda V \quad (1.14)$$

The $\lambda = 0$ corresponds to the unperturbed Hamiltonian \hat{H}_0 . At $\lambda = 1$, the system is said to be completely perturbed corresponding to the stationary states of the exact Hamiltonian. The exact states are obtained by carrying out Taylor series expansion of

these quantities around $\lambda = 0$.

$$\begin{aligned}\Psi_i^{(\lambda)} &= \Psi_i^0 + \lambda\Psi_i^1 + \frac{\lambda^2}{2!}\Psi_i^2 + \frac{\lambda^3}{3!}\Psi_i^3 + \dots \\ E_i^{(\lambda)} &= E_i^0 + \lambda E_i^1 + \frac{\lambda^2}{2!}E_i^2 + \frac{\lambda^3}{3!}E_i^3 + \dots\end{aligned}\tag{1.15}$$

In principle, MBPT can be used for any stationary state. However, in practice, it is mostly used for ground state calculations. Various methods are used to solve for the wavefunctions at various orders leading to different explicit expressions for the wavefunctions and the corresponding eigenvalues. The one developed by Brillouin and Wigner known as Brillouin-Wigner perturbation theory (BWPT) [20] and the other one developed by Rayleigh and Schrödinger known as Rayleigh-Schrödinger perturbation theory (RSPT) [18, 20, 21]. Both these approaches use Taylor series expansion around the solutions of the zeroth order part.

In BWPT, perturbation order at any order depends on exact ground state energy E_0 , which is priori not known. Therefore, one has to solve for total energy up to some order using an iterative procedure. In RSPT, the quantities in Eq. (1.14) and Eq. (1.15), are substituted in the Schrödinger equation. The terms with fixed power of V are then collected together and solved for energies and wavefunctions at various orders. It can be seen that, RSPT with MP partitioning leads to a size-extensive perturbation series. This feature was first proven by Brueckner [95] for first few orders in the context of infinite nuclear matter. However, he couldn't prove it for higher orders. Goldstone [96] using a diagrammatic approach showed that terms which have incorrect scaling (size-intensive), correspond to unlinked set of diagrams. He further showed that, the MP partitioned RSPT contains such unlinked diagrams which mutually cancel at every perturbation order, thereby leading to size-extensive series. This is the famous linked diagram theorem. The first application of diagrammatic approach was done by Kelly [97] for atoms.

Now a 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 wavefunction. 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.

1.4.3 Independent pair approximation

Electron correlation arises due to the interaction of two electrons of opposite spin. Thus, electron correlation may be considered as the effect of electron pairs. The simplest approximation is to consider only one electron pair at a time which reduces a N-electron problem to $\frac{N*(N-1)}{(2)}$ electron pairs. The interactions between the pairs are neglected and hence this is known as independent electron pair approximation (IEPA) method. In this approximation, total correlation energy is represented as the sum of the pair contributions, which are be obtained independently by solving effective two electron equations. This method was developed by Nesbet [98] and Sinanoglu [99] independently. Relation between IEPA and perturbation method has been extensively reviewed by Freed [100] and Robb [101]. The IEPA wave function for ij pair may be written as

$$\Psi_{ij} = \Phi_0 + \sum_{a<b} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \quad (1.16)$$

where i,j are the occupied and a,b are the virtual orbitals in HF determinant. Computationally, IEPA is equivalent to doing DCI for each pair separately and hence it is called pair-at-a-time CI. IEPA gives size-extensive results but it is not invariant to unitary transformation.

1.4.4 Coupled electron pair approximation

IEPA is based on two approximations : (a) neglect of the pair coupling terms and (b) assumption that the nonlinear terms cancel with part of the energy terms. W. Meyer [102] proposed a series of schemes which considered the coupling between the pairs. This is known as coupled electron pair approximation (CEPA). There are various versions of CEPA [103–105]. Some of them yields size-extensive results. It includes the interactions between the pairs but neglects most of the nonlinear terms.

1.4.5 Coupled-cluster theory

The Coupled-cluster (CC) method [24–26] has its conceptual origin in the pair correlation theories of Sinanoglu [99] and Nesbet [98]. The dynamical electron-correlation in CC wavefunction is brought in through an exponential wave-operator operating on the reference function, generally, the HF configuration. Since, the reference function is a single dominant configuration, the resulting CC is known as SRCC.

In CC, the ground state wavefunction of an N -electron system is obtained by action of an exponential wave-operator on a reference wavefunction, usually, the Hartree-Fock configuration.

$$|\Psi_0\rangle = \mathbf{e}^T |\Phi_0\rangle \quad (1.17)$$

Usually, the intermediate normalization scheme $\langle \Phi_0 | \Phi_0 \rangle = 1 = \langle \Phi_0 | \Psi_0 \rangle$ for the wavefunction. The operator T is cluster operator and like CI operators, it is a sum of one-electron excitation operator, two-electron excitation operator and so on up to N -electron excitation operators. In the language of second quantization, T is the sum of hole-particle creation operators.

$$T = T_1 + T_2 + \dots + T_N \quad (1.18)$$

with

$$\begin{aligned}
T_1 &= \sum_{i \in occ} \sum_{a \in virt} t_i^a \{a_a^\dagger a_i\} \\
T_2 &= \sum_{i,j \in occ} \sum_{a,b \in virt} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\} \\
&\text{and so on.}
\end{aligned} \tag{1.19}$$

The lowercase letters t are the amplitudes corresponding to the cluster operators T . In case of exact wavefunction, the cluster operators can be viewed as exponential parameterization of CI wavefunction with the following relationship between T and the C operators of CI wavefunction.

$$\begin{aligned}
C_1 &= T_1 \\
C_2 &= T_2 + \frac{1}{2!} T_1^2 \\
C_3 &= T_3 + T_1 T_2 + \frac{1}{3!} T_1^3 \\
C_4 &= T_4 + T_1 T_3 + \frac{1}{2!} T_1^2 T_2 + \frac{1}{2!} T_2^2 + \frac{1}{4!} T_1^4 \\
&\text{and so on.}
\end{aligned} \tag{1.20}$$

Above relationship between T and C is however, not valid in case of truncated CI and CC methods. Using the definition of Ψ given in Eq. (1.17), one can write the Schrödinger equation with normal-ordered Hamiltonian as

$$\hat{H}_N \mathbf{e}^T |\Phi_0\rangle = E_0^{corr} \mathbf{e}^T |\Phi_0\rangle \tag{1.21}$$

The above equation can be solved in various ways, which can be broadly classified into variational and non-variational methods leading to various types of CC ansatz. A traditional CC ansatz, also known as “normal” CC (NCC), is a non-variational one and can be obtained by two ways. One of them, the method of projection uses left projection of Eq. (1.21) by HF configuration and excited configurations to obtain the expressions for energy and the cluster amplitudes respectively. Application of generalized Wick’s

theorem leads to a set of connected set of equations for energy as well as the cluster amplitudes.

The same set of equations can also be obtained by similarity transformation method. In this method, we premultiply Eq. (1.21) by \mathbf{e}^{-T} to obtain

$$\mathbf{e}^{-T} \hat{H}_N \mathbf{e}^T |\Phi_0 \rangle = E_0^{corr} |\Phi_0 \rangle \quad (1.22)$$

Using the Campbell-Baker-Hausdorff formula the similarity transformed Hamiltonian \tilde{H} can be written as

$$\tilde{H} = \hat{H}_N + [\hat{H}_N, T] + \frac{1}{2!} [[\hat{H}_N, T], T] + \frac{1}{3!} [[[\hat{H}_N, T], T], T] + \dots \quad (1.23)$$

The Wick's theorem and fact that the cluster operators commute within themselves leads to two types of terms. One set of terms is graphically represented by connected diagrams, i.e. the diagrams with no vertex isolated from the rest and are referred to as connected terms. The another set of terms, the disconnected terms correspond to the disconnected diagrams. However, the disconnected terms mutually cancel out leading to a set of completely connected set of diagrams. It thus follows that

$$\mathbf{e}^{-T} \hat{H}_N \mathbf{e}^T = (\hat{H}_N \mathbf{e}^T)_C \quad (1.24)$$

The subscript C indicates the connectedness of the terms obtained from the contractions between \hat{H}_N and T . The connectedness ensures the size-extensivity and size-consistency. Due to two-body nature of \hat{H}_N , the series in Eq. (1.24) can be shown to terminate after the quartic power of T . The left hand side of Eq. (1.24) may be considered as a similarity transformed hamiltonian \tilde{H} .

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

This transformed Hamiltonian in general, is non-hermitian in nature. The ground state correlation energy is obtained by projecting Eq 1.22 with Φ_0 from the left. Projecting Eq

1.22 by the cited determinants, Φ^* , we get the equations for the cluster amplitudes, T . For the i^{th} cluster amplitudes, T_i , projection should be done with Φ_i^* . Thus, CC equations may be written as follows -

$$E_0^{corr} = \langle \Phi_0 | \tilde{H} | \Phi_0 \rangle = \langle \Phi_0 | (\hat{H}_N \mathbf{e}^T)_C | \Phi_0 \rangle \quad (1.25)$$

and

$$0 = \langle \Phi_i^* | \tilde{H} | \Phi_0 \rangle = \langle \Phi_i^* | (\hat{H}_N \mathbf{e}^T)_C | \Phi_0 \rangle \quad (1.26)$$

The Eq. (1.26) 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. (1.25).

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 number 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 ansatz is to define $T = T_1 + T_2$ leading to singles and doubles (SD) approximation. 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 ansatz can be further improved by perturbative or complete inclusion of triples, (CCSD(T) and CCSDT), quadrupoles (CCSDT(Q) and CCSDTQ), etc. These ansatz are seen to further accelerate the convergence the results towards the exactness.

1.4.6 Alternate SRCC approaches

As mentioned in 1.4.5, the Eq. (1.21) can be solved in various ways. We have seen that Normal CC (NCC) is a non-variational method. The non-variational nature makes it computationally unattractive for energy derivatives. There are several attempts to obtain stationary or variational CC method. The motivation behind this is to exploit Hellmann-Feynman theorem and $(2n + 1)$ rule for energy derivatives. Few of such attempts are discussed below.

Expectation value and unitary coupled-cluster ansatz

One of the attempts in variational CCM was to write the energy as an expectation value type hermitian functional $\langle \Psi_0^* | \hat{H} | \Psi_0 \rangle / \langle \Psi_0^* | \Psi_0 \rangle$. It follows

$$E = \frac{\langle \Phi_0 | \mathbf{e}^{T^\dagger} \hat{H} \mathbf{e}^T | \Phi_0 \rangle}{\langle \Phi_0 | \mathbf{e}^{T^\dagger} \mathbf{e}^T | \Phi_0 \rangle} \quad (1.27)$$

While T operators are hole-particle creation operators like in NCC; the T^\dagger being conjugate of T , indicate hole-particle destruction. The functional in Eq. (1.27) was named as expectation value CC (XCC) [106–108]. Although, the series given in Eq. (1.27) contains some disconnected terms, it was shown by Pal *et. al.* [106] that the disconnected part of the numerator is exactly cancelled by the denominator leaving behind a completely connected series.

$$E = \langle \Phi_0 | \mathbf{e}^{T^\dagger} H \mathbf{e}^T | \Phi_0 \rangle_C \quad (1.28)$$

However, the cancellation implicitly implies complete expansion of the power series of the numerator and denominator of Eq. (1.27) in terms of the cluster amplitudes. The cluster amplitudes are obtained by making the energy functional (Eq. 1.28) stationary with respect to T (or alternately T^\dagger).

It can be seen that the XCC functional is a nonterminating series. For practical applications, the series needs to be truncated. Pal *et. al.* [107] proposed a truncation of

the series after some fixed total power of T and T^\dagger . This truncation scheme is symmetric. However, this truncation of the functional did not yield a strict upper bound in energy. Later, Bartlett and Noga [108] proposed a truncation scheme for XCC based on the perturbation analysis. The terms whose leading contribution is greater than some fixed order n of perturbation, V (refer to section 1.4.2) are omitted in this truncation scheme and the functional is denoted by XCC(n). The disconnected terms in the equations of cluster amplitudes mutually cancel leading to a size-extensive functional although this truncation scheme is unsymmetric. Each XCC(n) has MBPT(n) as a special case.

Following Van Vleck [109] and Primas [110], Kutzelnigg [111] proposed an alternate approach in variational CCM called unitary CC (UCC). The functional is given by

$$|\Psi_0\rangle = \mathbf{e}^\sigma |\Phi_0\rangle \quad (1.29)$$

where σ is anti-hermitian. The special choice of σ may be $\sigma = T - T^\dagger$. The cluster amplitudes may be obtained using variational or non-variational amplitudes. The non-variational [108] approach is somewhat similar to NCC where, the set of equations can be obtained by replacing the T in the NCC equations by σ .

Conversely, UCC may be solved variationally as suggested by Kutzelnigg [111]. The expectation value like UCC functional can be written as

$$E = \frac{\langle \Phi_0 | \mathbf{e}^{-\sigma} \hat{H} \mathbf{e}^\sigma | \Phi_0 \rangle}{\langle \Phi_0 | \mathbf{e}^{-\sigma} \mathbf{e}^\sigma | \Phi_0 \rangle} \quad (1.30)$$

The denominator taken to all orders is identically equal to unity. This leads to a similarity transformed functional like NCC. However, the σ amplitudes are obtained variationally like in XCC. Bartlett and Noga used UCC(n) ansatz [108] analogous to XCC(n). However, unlike XCC(n), UCC(n) functional is symmetric.

Extended coupled-cluster method

As seen earlier, similarity transformed form of NCC ansatz given by Eq. (1.22) turns out to be a compact tool for developing algorithms for ground state energy. Arponen [113] extended this feature by adding one more similarity transformation on the Hamiltonian using hole particle destruction operators.

$$E_0^{corr} = \langle \Phi_0 | \mathbf{e}^S \mathbf{e}^{-\tau} \hat{H}_N \mathbf{e}^\tau \mathbf{e}^{-S} | \Psi_0 \rangle \quad (1.31)$$

The resulting ansatz was named as extended CC (ECC) [114–119]. In the above equation, the τ operators are the hole-particle creation operators like the T operators in NCC. The S operators on the other hand are hole-particle destruction operators analogous to the T^\dagger operators of XCC, although not conjugates of τ . A transformation on τ deals with new set of hole-particle creation operators T which absorb full contractions of S operators with singular τ operator. This leads to a double linked energy functional.

$$E_0^{corr} = \langle \Phi_0 | \mathbf{e}^S [\hat{H}_N \mathbf{e}^T]_L | \Psi_0 \rangle_{DL} \quad (1.32)$$

The subscript L indicates linking of T with \hat{H} . The subscript DL implies a ‘double’ linking [114] resulting from the transformation of τ to T . Double linking means that the S operators, if not directly connected to the Hamiltonian, shall contract with at least two distinct T operators. This ensures connectedness of the terms of the equations for S and T , which are obtained by making the energy stationary with respect to T and S respectively, thereby assuring the size-extensivity. The size-extensivity of ECC was tested long back by Piecuch and Bartlett [120].

1.5 Non-dynamical electron-correlation

The single reference (SR) methods discussed so far are applicable for the description of states dominated by single determinant which mainly include closed shell electronic

configuration. Certain open-shell states may well-described by UHF or ROHF methods. But, there are many situations in chemistry where the state involved contains dominant contributions from several determinants. This implies the presence of many other states energetically degenerate or nearly degenerate to the given state and strongly interacting with it. Examples of such situations include general open-shell states of atoms and molecules, excited, ionized and electron attached states, transition states, etc. Degenerate and quasi degenerate states characterized by a significant amount of non-dynamical electron correlation arising due to strong interaction between the dominant determinants.

For proper treatment of non-dynamical correlation, it is necessary to start with a specific reference space which includes all interacting determinants. This reference space, generally called model space, is usually constructed as a linear combination of strongly interacting determinants. Thus the zeroth order reference wave function may be presented as

$$\psi^{(0)} = \sum_{I=1}^M C_I \Phi_I \quad (1.33)$$

Methods which use multi-reference model space are commonly known as multi-reference (MR) methods. Parallel to this, there are some single reference based methods, like equation-of-motion coupled-cluster (EOMCC), [57–73] symmetry adapted cluster configuration interaction (SAC-CI) [55, 56] which are able to handle cases of quasi-degeneracy. In the next section, single-reference methods which are able to describe non-dynamical correlation, are described followed by multi-reference based methods.

1.6 Single-reference methods for non-dynamical correlation

1.6.1 Equation-of-motion methods

The Equations-of-motion(EOM) methods provide a compact tool to obtain difference energies directly rather than evaluating total energies of different states. In these

method, Rowe's [121] equation is solved for excitation operator $Q^\dagger(K)$ given by

$$Q^\dagger(K)|\Psi_0^U\rangle = |\Psi_K^W\rangle \quad (1.34)$$

The subscript K labels the excited state whereas W tells the total process, i.e. electron attachment (EA), ionization (IP) or simply, an electronic excitation (EE). Accordingly, $W = U \pm 1$ or $W = U$ respectively. Structure of the operator $Q^\dagger(K)$ depends on the process, i.e. IP, EA or EE. In case of EE, $Q^\dagger(K)$ is formed from a set of equal number of creation and annihilation operators. In case of EA, there will be one extra creation operator whereas, IP will require an extra annihilation operator in the set. For ease of explanation, we consider the example of electronic attachment. Let $|\Psi_0^N\rangle$ represent ground state wavefunction of an N -electron system. We consider addition of an electron to this system leading to K -th state of the resulting $(N + 1)$ -electron system. This can be described by action of $Q^\dagger(K)$ operator on $|\Psi_0^N\rangle$.

$$|\Psi_K^{N+1}\rangle = Q^\dagger(K)|\Psi_0^N\rangle \quad (1.35)$$

where,

$$Q^\dagger(K) = \sum_l t(K, l)T^\dagger(l) \quad (1.36)$$

To satisfy the above equation, the operator $T^\dagger(l)$ should be composed of union of sets of operators $\{a_a^\dagger\}$ that add an electron to orbital χ_a , operators $\{a_a^\dagger a_b^\dagger a_i\}$ which add an electron to orbital χ_a and excite another electron from χ_i to χ_b , operators $\{a_a^\dagger a_b^\dagger a_c^\dagger a_j a_i\}$ which, in addition to adding electron in orbital χ_a excite electrons from orbitals χ_i and χ_j to the orbitals χ_b and χ_c respectively, and so on. Both the systems satisfy the Schrödinger equation.

$$\hat{H}|\Psi_0^N\rangle = E_0^N|\Psi_0^N\rangle \quad (1.37)$$

$$\hat{H}|\Psi_K^{N+1}\rangle = E_K^{N+1}|\Psi_K^{N+1}\rangle \quad (1.38)$$

The operator \hat{H} is electronic Hamiltonian in second quantized form. Following Eq. (1.35), Eq. (1.37) and Eq. (1.38), one can easily show that

$$[\hat{H}, Q^\dagger(K)]|\Psi_0^N\rangle = (\hat{H}Q^\dagger(K) - Q^\dagger(K)\hat{H})|\Psi_0^N\rangle = (E_K^{N+1} - E_0^N)Q^\dagger(K)|\Psi_0^N\rangle \quad (1.39)$$

The Eq. (1.39) is an eigenvalue like equation. The appearance of the commutator $[\hat{H}, Q^\dagger(K)]$ leads to eigenvalue which is a direct energy difference obtained without rigorously solving for the exact energies E_0^N and E_K^{N+1} of the corresponding states. One can analogously obtain the equations for IP and EE.

The choice of the function $|\Psi_0^N\rangle$ in the EOM method leads to various EOM functionals. If HF wavefunction is used for describing the ground state and only one hole-particle creation operator is used, it is known as ‘‘Tamm-Dancoff approximation’’. If $Q^\dagger(K)$ consists of hole-particle creation as well as destruction operators, it is known as ‘‘Random phase approximation’’ [122]. Simons *et. al.* used Møller-Plesset (MP) [123] expansion for the wavefunction. The EOM approach using CC ansatz led to the EOM-CC [57–65, 69, 70] methods and are now, very commonly used for IP, EA and EE calculations. The more recent similarity transformed (ST) EOM-CC is also an efficient technique for difference energy calculations.

1.6.2 Symmetry adapted cluster configuration interaction

In normal coupled cluster method, wave-function Ψ is presented as

$$\Psi = \exp(T)\Phi_0 \quad (1.40)$$

where Φ_0 is reference determinant and T is the sum of cluster amplitudes. In symmetry adapted cluster configuration interaction (SAC-CI) [55, 56] method, the operator T is expanded by means of the excitation operators S^+ as

$$T = \sum_i C_i S_i^+ + \sum_{i>j} C_{ij} S_{ij}^+ + \dots \quad (1.41)$$

where C terms are the coefficients. The main effects of the first and second terms of T are to improve basic orbitals and pair-correlations, respectively. Merit of this formulation is that the freedom in the choice of S^+ is much wider than that permitted in the conventional orbital theory.

1.7 Multi-reference based methods

1.7.1 Multi-configurational self-consistent field

Multi-configurational self-consistent field (MCSCF) [124, 125] is the first multi-reference method in quantum chemistry which used to generate qualitatively correct reference states of molecules in cases where single reference methods are not adequate. It uses a linear combination of configuration state functions (CSF) or configuration determinants to approximate the exact electronic wave function of an atom or molecule. In an MCSCF calculation, the set of coefficients of both the CSFs or determinants and the basis functions in the molecular orbitals are varied to obtain the total electronic wave function with the lowest possible energy. This method can be considered a combination between configuration interaction and Hartree-Fock.

MCSCF wave functions are often used as reference states for i Multireference configuration interaction (MRCI) or multi-reference perturbation theories like Complete Active Space Perturbation Theory (CASPT2). These methods can deal with extremely complex chemical situations and, if computing power permits, may be used to reliably calculate molecular ground- and excited states if all other methods fail.

1.7.2 Multi-reference configuration interaction method

Multi-reference configuration interaction (MRCI) [30, 126–129] method is one of the standard benchmark methods in quantum chemistry. It is a straightforward extension of the SRCI method to multi-reference situation. In this method, the reference function is taken as linear combination of several strongly interacting configurations. The dynamical correlation is taken care by carrying out excitations on each determinant in the reference space through a linear wave-operator. The wave function for MRCI using SD approximation may be written as

$$\Psi_{MRCI-SD} = \sum_{I=l}^M C_I \Phi_I + \sum_S C_S \Phi_S + \sum_D C_D \Phi_D \quad (1.42)$$

where, Φ_S and Φ_D are respectively singly and doubly excited determinants. In general, reference space contains singly and doubly excited determinants which includes the effect of triple and quadruple excitations in the final MRCI wave-function.

As with truncated CI methods, none of the MRCI methods are size-extensive. Attempts for size-consistent MRCI methods lead to multi-reference generalizations of CEPA method (MR-CEPA) [130–132]. The MR-ACPF method of Gdanitz and Ahlrichs [133], MR-AQCC method of Szalay and Bartlett [134] are some examples of such methods. All these methods are inherently state-selective and lie between MRCI and state-selective MRCC methods.

1.7.3 Multi-reference perturbation theories

The multi-reference perturbation theory (MRPT) [31, 32] closely resembles with the MBPT theory except for the MR character of the model space. MRPT approaches can be divided into two categories [135]. One of approach uses perturbative construction of an effective Hamiltonian defined over the reference space. Other method closely follow the single reference perturbation theory. A zeroth order wavefunction qualitatively

describing the desired state is first constructed by diagonalizing the Hamiltonian over the model space, usually through a multi-configuration self-consistent field (MCSCF) calculation. This is then used to construct the zeroth order Hamiltonian, which then defines perturbation. The perturbative expansion over zeroth order wavefunction is used to obtain the corrections to the wavefunction and energies at various order. This is a state-specific approach (one state at a time), usually referred to as “diagonalize-then-perturb” approach.

Another approach in MRPT includes “perturb-then-diagonalize” methods popularly known as quasi-degenerate perturbation theories (QDPT) [33, 34]. These methods involve perturbative construction of an effective Hamiltonian defined over a model space whose diagonalization yields approximate energies and wavefunctions of one or more states.

1.7.4 Effective Hamiltonian approach

Effective Hamiltonian approach is an alternative way to develop multi-reference method and treat non-dynamical electron correlation. In this method, N -electron Hilbert space is partitioned into smaller M -dimensional model space P and its complement space Q . The model space is spanned by a set of M determinants $\{\Phi_I, I = 1, \dots, M\}$ and the complement space is spanned by $\{\Phi_I, I = M + 1, \dots, \infty\}$. The model space is assumed to be an approximation to some M -dimensional target space P spanned a set of M quasi-degenerate exact states $\{\Psi_A, A = 1, \dots, M\}$ of the full Hamiltonian, \hat{H} , whose energies are $\{\varepsilon_A, A = 1, \dots, M\}$.

In this approach, an effective operator is constructed whose eigen vectors are model functions but eigen values are exact. This operator is called effective Hamiltonian H_{eff} .

Effective Hamiltonian is generally defined by Bloch equation [136, 137] written as follows

$$\hat{H}\Omega P = \Omega H_{eff} P \quad (1.43)$$

The solution of Bloch equation requires the projection with a complete set of states i.e. with both P and Q . This set of equations implicitly define Ω and H_{eff} though the equations are coupled.

1.7.5 Multi-reference coupled-cluster methods

The formation of multi-reference coupled cluster (MRCC) theories [35–38, 43, 45, 46, 74, 138, 139] are more or less independent of the underlying perturbative structure. An exponentially parametrized wave-operator Ω is used to obtain size-extensive results. There are two classes of MRCC methods, one is state selective MRCC method [40] and other uses multi-root effective Hamiltonian intermediate. In multi-root MRCC method, like effective Hamiltonian approach, a model space is constructed taking strongly acting configurations. If the model space contains all possible configurations, it is called complete model space (CMS). With such model space, it is easy to exponentially parametrized Ω to satisfy intermediate normalization. This classes of MRCC are subdivided into two classes depending upon the way how the non-dynamical correlation is taken care. The first one, proposed by Jezioroski and Monkhorst [138], is referred to as state-universal or Hilbert-space(HS) MRCC and the other is called as valence universal or Fock-space (FS) MRCC [36, 37, 43, 45, 46, 51, 52, 74]. Details of these two methods are discussed bellow.

Hilbert-space multi-reference coupled-cluster method

In Hilbert space approach, the wave operator is expressed as

$$\Omega = \sum_K e^{T(K)} P_K \quad (1.44)$$

where P is projection operator, which is an idempotent operator and the cluster operator, T , should be such that none of the T_n operators can produce excitations within the model space. The general expression for the K^{th} reference determinant in HSMRCC is given as

$$[H_0, e^{T(K)}]|\phi_K\rangle = V e^{T(K)}|\phi_K\rangle - \sum_L e^{T(L)}|\phi_L\rangle \langle \phi_L | V e^{T(K)}|\phi_K\rangle \quad (1.45)$$

where K and L run over all references configurations. Projecting Eq. (1.45) onto the subspace of the singly and doubly excited configurations with respect to ϕ_k we obtain MRCC equations as for single excitation amplitudes

$$\begin{aligned} \langle \phi_i^a(K) | [e^{T(K)}, H_0] | \phi_K \rangle &= \langle \phi_i^a(K) | V e^{T(K)} | \phi_K \rangle \\ &- \sum_L \langle \phi_i^a(K) | e^{T(L)} | \phi_L \rangle \langle \phi_L | V e^{T(K)} | \phi_K \rangle \end{aligned} \quad (1.46)$$

and for double excitation amplitudes

$$\begin{aligned} \langle \phi_{ij}^{ab}(K) | [e^{T(K)}, H_0] | \phi_K \rangle &= \langle \phi_{ij}^{ab}(K) | V e^{T(K)} | \phi_K \rangle \\ &- \sum_L \langle \phi_{ij}^{ab}(K) | e^{T(L)} | \phi_L \rangle \langle \phi_L | V e^{T(K)} | \phi_K \rangle \end{aligned} \quad (1.47)$$

This provides a starting point for the derivation of explicit recursive formula for t_1, t_2, \dots coefficients. This approach is conceptually similar to the single reference method. If we suppress the second term on the right hand side of Eqs (1.46,1.47) then from the point of view of the particular reference ϕ_K we obtain the single reference equations. It is obvious that, certain amplitudes which are responsible for excitations within the model space, are excluded. The final equations for t_i^a and t_{ij}^{ab} are expressed as

$$D_i^a t_i^a(K) = \langle \phi_i^a(K) | V e^{T(K)} | \phi_K \rangle_C - \sum_{L \neq K} (\langle \phi_i^a(K) | e^{T(L)} | \phi_L \rangle H_{LK})_C \quad (1.48)$$

$$\begin{aligned}
D_{ij}^{ab} t_{ij}^{ab}(K) &= \langle \phi_{ij}^{ab}(K) | V e^{T(K)} | \phi_K \rangle_C - \sum_{L \neq K} (\langle \phi_{ij}^{ab}(K) | e^{T(L)} | \phi_L \rangle H_{LK})_C \\
&\quad - \sum_{L \neq K} (t_i^a(K) - t_i^a(L)) (\phi_j^b(K) | e^{T(L)} | \phi_L \rangle H_{LK})_C
\end{aligned} \tag{1.49}$$

State selective multi-reference coupled-cluster method

In state selective multi-reference coupled-cluster (SSMRCC) [40, 140–144] method exponential wave-operator, e^T , is partitioned into two parts, $e^{T^{(int)}}$ and $e^{T^{(ext)}}$. $e^{T^{(int)}}$ acts on a suitably chosen single-determinant reference function which generates the model space reference function, $|\Phi^{(int)}\rangle$, which is a linear combination of reference determinants. $e^{T^{(ext)}}$ produces excitations outside the model space. Thus, exact wave function is generated as

$$|\Psi\rangle = e^{T^{(ext)}} |\Phi^{(int)}\rangle = e^{T^{(ext)}} e^{T^{(int)}} |0\rangle \tag{1.50}$$

$T^{(int)}$ and $T^{(ext)}$ commute as both of them are excitation operator of same reference function. The SSMRCC correlation energy expression and equations for T amplitudes are as follows

$$\langle 0 | [H_N \exp T^{(ext)} \exp T^{(int)}] | 0 \rangle = E_{corr} \tag{1.51}$$

$$\langle \Phi^* | [H_N \exp T^{(ext)} \exp T^{(int)}] | 0 \rangle = 0 \tag{1.52}$$

here, intermediate normalization ie, $\langle \Psi | 0 \rangle = 1$ is used. Φ^* represents any specific excited configuration. H_N is the normal order Hamiltonian ($H_N = H - \langle 0 | H | 0 \rangle$) which is the sum of one-body (F_N) and two-body (V_N) operators.

In order to more effectively handle the general quasi-degeneracy problem, a linearized form for the internal operator, $e^{T^{(int)}}$, is used keeping external operator as such [145]. The resulting ansatz assumes the form given bellow.

$$|\Psi\rangle = \exp T^{(ext)} (1 + C^{(int)}) |0\rangle \tag{1.53}$$

In this case, the equations for the amplitudes are linear in terms of $C^{(int)}$. In general, if $T^{(int)}$ includes all possible excitations within the active orbital space, the $\exp T^{(int)} |0\rangle$

and $(1 + C^{(int)})|0\rangle$ wave-functions are completely equivalent and only practical reasons may determine which approach will be more effective and convenient in a particular case.

Fock-space multi-reference coupled-cluster method

As mentioned earlier, FSMRCC [36, 37, 43, 45, 46, 50–52, 74] is based on the concept of a common vacuum. We choose an N -electron RHF configuration as vacuum, which defines the holes and particles. In the Fock-space, the model space determinants contain h -holes and p -particles distributed within a set of what are termed as active holes and active particles, usually around the fermi level. We denote the above p -active particle, h -active hole model space determinant by $\{\Phi_i^{(p,h)}\}$. Thus, the model space of a (p, h) valence Fock-space can be written as

$$|\Psi_\mu^{(p,h)}\rangle = \sum_i C_{i\mu}^{(p,h)} |\Phi_i^{(p,h)}\rangle \quad (1.54)$$

The projection operator for model space is defined as

$$P^{(p,h)} = \sum_i |\Phi_i^{(p,h)}\rangle \langle \Phi_i^{(p,h)}| \quad (1.55)$$

The orthogonal component of the model space, i.e. the virtual space is defined as

$$Q = 1 - P \quad (1.56)$$

The dynamical electron correlation arises due to comparatively weak interactions of the model-space configurations with the virtual space configurations. This interaction is brought in through a universal wave operator Ω which is parameterized such that the states generated by its action on the reference function satisfy Schrödinger equation. To generate the exact states for the (p, h) valence system, the wave operator must generate all valid excitations from the model space. Subsequently, Ω should contain cluster operators $\{\tilde{T}^{(p,h)}\}$ which are defined as follows

$$\tilde{T}^{(p,h)} = \sum_{k=0}^p \sum_{l=0}^h T^{(k,l)} \quad (1.57)$$

The superscripted bracket in the right hand side of the above expression indicates that the cluster operator T is capable of destroying exactly k active particles and l active holes, in addition to creation of holes and particles. The $\tilde{T}^{(p,h)}$ operator subsumes all such lower $T^{(k,l)}$ operators. Using these operators, the Ω is defined as follows.

$$\Omega = \{e^{\tilde{T}^{(p,h)}}\} \quad (1.58)$$

The brace-bracket in Eq. (1.58) indicates normal ordering of the cluster-operators. The Schrödinger equation for the manifold of quasi-degenerate states can be written as

$$H|\Psi_i^{(p,h)}\rangle = E_i|\Psi_i^{(p,h)}\rangle$$

which leads to

$$H\Omega\left(\sum_i C_{i\mu}^{(p,h)}\Phi_i^{(p,h)}\right) = E_\mu\Omega\left(\sum_i C_{i\mu}^{(p,h)}\Phi_i^{(p,h)}\right) \quad (1.59)$$

The effective Hamiltonian for (p, h) valence system can be defined such that

$$\sum_j (H_{eff}^{(p,h)})_{ij} C_{j\mu} = E_\mu C_{i\mu} \quad (1.60)$$

$$(H_{eff}^{(p,h)})_{ij} = \langle \Phi_i^{(k,l)} | \Omega^{-1} H \Omega | \Phi_j^{(k,l)} \rangle$$

which can be written as

$$H_{eff}^{(p,h)} = P^{(p,h)} \Omega^{-1} H \Omega P^{(p,h)} \quad (1.61)$$

Problem of defining H_{eff} using Eq. 1.61 arises because inverse of wave-operator, Ω , may not exist. More general definition of H_{eff} is given by Bloch and Lindgren which is, in general, known as Bloch equation (see Eq. 1.43). Bloch equation may be considered as a modified form of Schrödinger equation.

The Bloch-Lindgren approach not only eliminates the requirement of Ω^{-1} , but also provides an important criterion the effective Hamiltonian must fulfill. The effective Hamiltonian is, in general, non-hermitian. Mainly two approaches are used to obtain

Ω and the effective Hamiltonian. One of them, known as Bloch projection approach, involves left projection of above equation by P and Q .

$$\begin{aligned} P^{(k,l)}[H\Omega - \Omega H_{eff}^{(k,l)}]P^{(k,l)} &= 0 \\ Q^{(k,l)}[H\Omega - \Omega H_{eff}^{(k,l)}]P^{(k,l)} &= 0 \\ & ; \forall k = 0, \dots, p; l = 0, \dots, h \end{aligned} \quad (1.62)$$

The normalization condition is specified indirectly through parameterization of Ω . In case of complete model spaces (CMS), the intermediate normalization is commonly employed.

The diagonalization of the effective Hamiltonian within the P space gives the energies of the corresponding states and the left and the right eigen vectors.

$$\begin{aligned} H_{eff}^{(p,h)}C^{(p,h)} &= C^{(p,h)}E \\ \tilde{C}^{(p,h)}H_{eff}^{(p,h)} &= E\tilde{C}^{(p,h)} \end{aligned} \quad (1.63)$$

$$\tilde{C}^{(p,h)}C^{(p,h)} = C^{(p,h)}\tilde{C}^{(p,h)} = 1 \quad (1.64)$$

Because of normal ordering, the contractions amongst different cluster operators within the exponential are avoided, leading to partial hierarchical decoupling of cluster equations. This is commonly referred to as sub-system embedding condition (SEC). The lower valence cluster equations are completely decoupled from the higher valence cluster equations because of SEC. Hence, the Bloch equations are solved progressively from the lowest valence $(0, 0)$ sector upwards up to (p, h) valence sector.

1.8 Atomic and molecular properties

According to the postulates of quantum mechanics, wave-function contains all information about the system. Thus, in principle, all properties of a system can be extracted using

it. Any property a of any system at any state, which is described by a wave-function Ψ , is the expectation value of the corresponding property operator, \hat{A} , which may be given as

$$a = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.65)$$

Molecular properties such as dipole moment can be computed using this approach which is not possible for several other molecular properties, e.g. polarizability, transition moment, etc. Electric polarizability is related to the electric dipole moment induced when molecule is placed in an external electric field. Thus, electric polarizability is a measure of how a molecule responds to the external electric field and hence, is referred to as response properties. To define response properties, Hellmann-Feynman theorem [?] is used. A general expression is as follows,

$$\frac{\partial E(p)}{\partial p} = \frac{\langle \Psi(p) | \frac{\partial \hat{H}(p)}{\partial p} \hat{A} | \Psi(p) \rangle}{\langle \Psi(p) | \Psi(p) \rangle} \quad (1.66)$$

Here, $\Psi(p)$ is an exact eigenvector of $\hat{H}(p)$. For response properties, perturbed Hamiltonian is used as follows,

$$\hat{H}(\vec{F}) = \hat{H} - \vec{d} \bullet \vec{F} = \hat{H} - \sum_{i=1}^3 d_i F_i \quad (1.67)$$

Where, \vec{F} is the applied field. Here, it should be mentioned that , the applied field should be weak so that time-independent perturbation should be used. For weak field perturbation, Taylor series expression may be used for $E(\vec{F})$, $\hat{H}(\vec{F})$ and $\Psi(\vec{F})$ around the zero field strength. This procedure leads to identify various higher order response properties. For example, electric dipole moment is the first-order energy derivative, dipole polarizability is the second-order energy derivative, hyper-polarizability is the third-order energy derivative, with respect to the electric field perturbation. For defining frequency-dependent properties, a time-dependent weak perturbation is required.

1.9 Linear response method for molecular properties

Hamiltonian of the 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 linear response(LR).

$$\hat{H}(g) = \hat{H}^{(0)} + g\hat{O} \quad (1.68)$$

In the above equation, $\hat{H}^{(0)}$ is total electronic Hamiltonian in absence of external perturbation. For uniform external electric field, \hat{O} will be electric dipole moment operator. If the quantities $\Upsilon = \{E, \Psi\}$ is expressed as a Taylor series expansion of g as

$$\Upsilon(g) = \sum_k \frac{1}{k!} g^k \Upsilon^{(k)} \quad (1.69)$$

then, $\Upsilon^{(k)}$ will be 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 Schrödinger equation for the system of interest at various field values and obtain the numerical derivatives of energy by finite difference method. This approach is known as finite field (FF) approach and requires very accurate evaluation of energy, although, no computational developments are required. Alternately, the molecular properties may be obtained analytically. In analytic method, explicit evaluation of energy derivatives are required to obtain molecular properties. It is known that,

an exact wavefunction, which is variationally optimized, follows Hellmann-Feynman theorem.

$$\frac{\partial}{\partial g} \int \Psi(g) \hat{A}(g) \Psi(g) d\tau = \int \Psi(g) \frac{\partial \hat{A}}{\partial g} \Psi(g) d\tau \quad (1.70)$$

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

1.9.1 NCC linear response

The NCC-LR was initiated by Monkhorst [28]. In presence of a uniform external field, the NCC wavefunction can be expanded in Taylor series of g as given in Eq. (1.69). The expressions for derivatives of energy and wavefunctions are obtained by differentiating Eq. (1.25) and Eq. (1.26) 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 derivatives of correlation energy and cluster amplitudes respectively, neglecting the orbital relaxation are given below.

$$\langle \Phi_0 | e^T \{ \hat{O} + [H, T^1] \} e^T | \Phi_0 \rangle = E^{(1)} \quad (1.71)$$

$$\langle \Phi^* | e^T \{ \hat{O} + [H, T^1] \} e^T | \Phi_0 \rangle = 0 \quad (1.72)$$

The NCC-LR method described above is conceptually very simple and straightforward. However, for each mode of perturbation, one has to obtain the wavefunction

derivatives which makes the method practically cumbersome, particularly for higher order properties.

1.9.2 Effective techniques for SRCC linear response

NCC-LR can be solved more efficiently by circumventing the solution of wavefunction derivatives to the extent possible. Mainly two techniques have been proposed to achieve this.

The Z-vector technique

Based on Dalgarno's interchange theorem [146], Bartlett and co-workers [29, 147, 148] introduced the Z-vector technique in NCC-LR. The idea was taken from Handy and Schaefer [149] who used the technique for analytical derivatives for CI method. We rewrite Eq. (1.71) and Eq. (1.72) in a compact form as

$$E_0^{corr(1)} = Y^T T^{(1)} + Q(\hat{O}) \quad (1.73)$$

$$0 = AT^{(1)} + B(\hat{O}) \quad (1.74)$$

where,

$$\begin{aligned} Y^T T^{(1)} &= \langle \Phi_0 | (\hat{H}_N \mathbf{e}^T T^{(1)})_C | \Phi_0 \rangle \quad ; \quad Q(\hat{O}) = \langle \Phi_0 | (\hat{O} \mathbf{e}^T)_C | \Phi_0 \rangle \\ AT^{(1)} &= \langle \Phi_I | (\hat{H}_N \mathbf{e}^T T^{(1)})_C | \Phi_0 \rangle \quad \text{and} \quad B(\hat{O}) = \langle \Phi_I | (\hat{O} \mathbf{e}^T)_C | \Phi_0 \rangle \end{aligned} \quad (1.75)$$

We introduce a perturbation independent vector Z^T as

$$Z^T A = Y^T \quad (1.76)$$

Following Eq. (1.76) and Eq. (1.74) and substituting them into Eq. (1.73), it follows,

$$E_0^{corr(1)} = Z^T B(\hat{O}) + Q(\hat{O}) \quad (1.77)$$

The above equation for first derivative of energy is independent of wavefunction derivative. Thus, one has to solve only one extra set of perturbation independent amplitudes, i.e. the Z-vectors, defined by Eq. (1.76), in addition to the cluster amplitudes, making the procedure of obtaining first derivatives of energy more efficient.

Constrained Variational Approach

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 constrained variational approach (CVA) of Jørgensen and co-workers [150–152] extends the benefits of the Z-vector technique for higher order derivatives of energy. Based on the method of Lagrange’s undetermined multipliers, CVA involves construction of lagrangian as follows.

$$\mathfrak{S} = \langle \Phi_0 | (\hat{H} \mathbf{e}^T)_C | \Phi_0 \rangle + \sum_{I \neq 0} \lambda_I \langle \Phi_I | (\hat{H} \mathbf{e}^T)_C | \Phi_0 \rangle \quad (1.78)$$

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 \mathfrak{S} leads to equations for λ -vectors, which are same as Z-vectors. The CVA formulation transparently extends the cost-effectivity for higher order derivatives. While the cluster operators obey $(2n + 1)$ -rule for energy derivatives, the λ -vectors follow $(2n + 2)$ -rule [151, 152].

1.9.3 Linear response of stationary CC ansatz

As discussed earlier, the main advantage of the stationary methods is applicability of the generalized Hellmann-Feynman theorem. The XCC/UCC response approach was developed by Pal [153] and extensively used for obtaining static properties [154–156] of molecules. In this method, the energy functional and its response are expressed in

terms of cluster amplitudes and their derivatives. The energy and cluster amplitudes in presence of external field are expanded in Taylor series of the field. It was shown by Pal and co-workers [154, 155] that if cluster amplitudes and their derivatives are truncated to uniform degree, then the stationarity condition $\partial E^{(i)}/\partial T^{(j)} = 0$ leads to identical set of equations for a fixed value of $(i - j)$. The cluster amplitude derivatives of particular order can thus be obtained by making the derivative energy functional of that order stationary with respect to the unperturbed amplitudes. The stationarity leads to $(2n + 1)$ -rule for derivative energy calculation. However, due to disconnected terms in the equations of cluster amplitudes and derivatives, these methods suffer from loss of size-extensivity. Pal and co-workers also attempted to extend the stationary response methods for multi-determinantal CC [157].

While, the XCC and UCC functionals suffer from loss of size-extensivity due to disconnected terms in cluster equations, the double-linked form of ECC functional ensures the size-extensivity even for the energy derivatives. ECC has therefore, emerged as a state-of-the-art method for obtaining molecular properties. Pal and co-workers extensively used ECCSD response for molecular electric properties [117, 118].

1.9.4 Linear response to HSMRCC

Extension of algebraic Z-vector method is difficult for higher order energy derivatives, although it has been pursued in SRCC context by Slater and co-workers [158] to obtain the expression for the second derivative. However, it is better to go over to constrained variation approach [159]. The approach generalizes the Z-vector method to all orders retaining the simplicity of HSMRCC method. For this method, a functional is constructed with Lagrange multipliers for any particular state with certain constraints. This functional leads to equations for Lagrange multipliers corresponding to cluster amplitude equation. $(2n+1)$ rule is valid for cluster amplitudes and model space coefficients

while $(2n+2)$ rule is valid for Lagrange multipliers.

If, the set of cluster amplitudes for all vacua is denoted by T , the set of model space coefficients for the i^{th} state is denoted by C_i and Lagrange multipliers are denoted by Λ , then, the following equations may be written.

$$\begin{aligned}
T &= \{T_\mu \forall \mu\} \\
C_i &= \{\tilde{C}_{i\mu}, C_{\mu i} \forall \mu\} \\
\Lambda &= \{\Lambda_\mu \forall \mu\} \\
\Theta &= \{T, C_i, \Lambda, E_i\} \tag{1.79}
\end{aligned}$$

where E_i is the energy for the i^{th} state. The Lagrange functional corresponds to HSM-RCC equations is as follows.

$$\mathfrak{S}(\Theta) = \sum_{\mu, \nu} \tilde{C}_{i\nu} C_{\mu i} H_{eff}^{\nu\mu} + \sum_{q, \eta} \lambda_q(\eta) E_q(\eta) - E \left(\sum_{\mu} \tilde{C}_{i\mu} C_{\mu i} - 1 \right) \tag{1.80}$$

To derive expressions for various order derivatives, a small perturbation $H^{(1)}$ with strength parameter g is introduced into the Hamiltonian H as

$$H(g) = H + gH^{(1)} \tag{1.81}$$

Since Θ is determined at all strengths of perturbation g , the functional \mathfrak{S} becomes a function of g , denoted by $\mathfrak{S}(g, \Theta)$. Using Taylor series expansion we can write

$$\mathfrak{S}(g, \Theta) = \mathfrak{S}^{(0)} + g\mathfrak{S}^{(1)} + \frac{1}{2!}g^2\mathfrak{S}^{(2)} + \frac{1}{3!}g^3\mathfrak{S}^{(3)} + \dots \tag{1.82}$$

It should be mentioned that $\mathfrak{S}^{(n)}$ is a functional of quantities $\{\Theta^{(M)} m = 0, n\}$. All response equations upto a required order n can be derived by making the functionals $\{\mathfrak{S}^{(k)} k = 0, n\}$ stationary with respect to $\{\Theta^{(m)} m = 0, n(m \leq k)\}$. This leads to the following equation

$$\frac{\partial \mathfrak{S}^{(k)}}{\partial \Theta^{(m)}} = 0, \forall k, \forall m, (m \leq k), (k = 0, n) \tag{1.83}$$

To evaluate different parameters, the equations obtain by making $\frac{\partial \mathfrak{S}}{\partial \Theta}$ equal to 0, should be solved. Equations for Λ may be given as

$$\sum_{\eta, q} \lambda_q(\eta) [E_q(\eta)]_{T_i \mu} = - \sum_{\nu} \tilde{C}_{i\nu} C_{\mu i} \langle \Phi_{\nu} | e^{-T_{\mu}} H e^{T_{\mu}}, T_i(\mu) | \Phi_{\mu} \rangle \forall, \mu \quad (1.84)$$

The expression for the first and the second order energy derivatives are as follows

$$\mathfrak{S}^{(1)} = \sum_{\mu, \nu} \tilde{C}_{i\nu} C_{\mu i} [H_{eff}^{\nu\mu(1)}]_{T^{(0)}} + \sum_{q, \eta} \lambda_q(\eta) [E_q^{(1)}(\eta)]_{T^{(0)}} \quad (1.85)$$

and

$$\begin{aligned} \mathfrak{S}^{(2)} = & \sum_{\mu, \nu} \tilde{C}_{i\nu} C_{\mu i} [H_{eff}^{\nu\mu(2)}]_{T^{(1)}} + \sum_{q, \eta} \lambda_q(\eta) [E_q^{(2)}(\eta)]_{T^{(1)}} \\ & - 2 \left(\sum_{\mu, \nu} \tilde{C}_{i\nu}^{(1)} C_{\mu i}^{(1)} H_{eff}^{\nu\mu} - E \sum_{\mu} \tilde{C}_{i\mu}^{(1)} C_{\mu i}^{(1)} \right) \end{aligned} \quad (1.86)$$

Implementation of linear response techniques in HSMRCC frame work are going on. Chattopadhyay and Mukhopadhyay [160] implemented it to compute low-lying potential energy surface. Pittner and Šmydke [161] implemented for gradient calculation.

1.9.5 Linear response to FSMRCC

The LR in FSMRCC framework was initiated by Pal [74] and then implemented by Pal and co-workers [75] for dipole moments of doublet radicals and excited states of closed-shell molecules. The method is non-variational and involves explicit differentiation of Bloch equation with respect to uniform external field. In presence of time-independent uniform external field, the parameters $\Upsilon = \{H_{eff}^{(p,h)}, C^{(p,h)}, \tilde{C}^{(p,h)}, E, \Omega\}$ become perturbation dependent and can be expanded in Taylor series of g .

$$\Upsilon(g) = \Upsilon^{(0)} + g\Upsilon^{(1)} + \frac{1}{2!}g^2\Upsilon^{(2)} + \frac{1}{3!}g^3\Upsilon^{(3)} + \dots \quad (1.87)$$

The differentiation of the Bloch equations following left projections by model space and virtual space configurations with respect to g yields wavefunction derivatives

and derivative effective Hamiltonian. The equations are linear in the perturbation dependent quantities. It is interesting to note that the homogeneous parts of the Ω derivative equations are identical to the linear homogeneous part of the undifferentiated cluster equations. The SEC transparently holds at every order. The method provides multiple roots of derivative effective-Hamiltonian which can be obtained simultaneously by solving following equations.

$$\sum_i \{ (H_{eff}^{(1)})_{ji} C_{i\mu}^{(0)} + (H_{eff}^{(0)})_{ji} C_{i\mu}^{(1)} \} = E_{\mu}^{(1)} C_{j\mu}^{(0)} + E_{\mu}^{(0)} C_{j\mu}^{(1)} \quad (1.88)$$

However, due to its non-variational nature, the method does not obey the generalized Hellman-Feynman theorem for energy derivatives. Therefore, the evaluation of n^{th} order energy derivatives demands the knowledge of cluster amplitudes and their derivatives up to n^{th} order.

There have been various attempts in MRCC, along the lines of SRCC, to eliminate the cumbersome solution of wavefunction derivatives for different modes of perturbation. The Z-vector formalism by Pal and co-workers [162] is one of them. Szalay [82] formulated the CVA technique in FSMRCC but the method was applicable only for CMS. Later, Pal and co-workers [80] independently formulated the CVA-FSMRCC for general IMS and showed that the functional simplifies to the one proposed by Szalay [82] if applied for CMS and QMS. The CVA-FSMRCC method of Pal and co-workers provides response of a specific root of the multiple roots of FSMRCC. One has to project a single desired state (root of effective Hamiltonian) for doing constrained variation. In FSMRCC context, the energy of a specific state of the (p, h) FS sector is given by

$$E_{\mu} = \sum_{ij} \tilde{C}_{\mu i}^{(p,h)} (H_{eff})_{ij}^{(p,h)} C_{j\mu}^{(p,h)} \quad (1.89)$$

We construct the Lagrangian to minimize the energy expression given above, with

the constraint that the MRCC equations [Eq. (1.62)] are satisfied for the state μ .

$$\begin{aligned}
\mathfrak{S} = & \sum_{ij} \tilde{C}_{\mu i}^{(p,h)} (H_{eff})_{ij}^{(p,h)} C_{j\mu}^{(p,h)} \\
& + \sum_{k=0}^p \sum_{l=0}^h \{ P^{(k,l)} \Lambda^{(k,l)} P^{(k,l)} P^{(k,l)} [H\Omega - \Omega H_{eff}^{(k,l)}] P^{(k,l)} \\
& + P^{(k,l)} \Lambda^{(k,l)} Q^{(k,l)} Q^{(k,l)} [H\Omega - \Omega H_{eff}^{(k,l)}] P^{(k,l)} \} \\
& + E_{\mu} \left[\sum_{ij} \tilde{C}_{\mu i}^{(p,h)} C_{j\mu}^{(p,h)} - 1 \right] \tag{1.90}
\end{aligned}$$

In this thesis, we present the computational development of CVA-FSMRCC with SD approximation (CVA-FSMRCCSD) for molecules in doublet and triplet states. The procedure of solution of Eq. (1.90) and the finer details regarding simplifications in certain cases will be discussed in appropriate places.

1.10 Overview of this thesis

This thesis focuses on the development and implementation of Lagrangian based FSMRCC method for calculation of electric properties of excited states and doublet radicals. In particular, first calculation of polarizabilities and first hyper-polarizabilities of radicals are presented using the CVA-FSMRCCSD approach. Similarly, polarizabilities and first hyper-polarizabilities of low-lying excited states have also been presented.

In chapter 2, CVA-FSMRCCSD theory and the Lagrange formulation have been discussed for open shell doublet molecules and the expressions for first- and second-order energy derivatives are given. Also analytic dipole moments and dipole polarizabilities of Oxygen mono-fluoride and Nitrogen dioxide using CVA-FSMRCCSD method are presented.

Chapter 3 includes FSMRCCSD method for calculation of excited state properties of closed shell molecules. Theoretical details have been given with description of code developed. Application of this method for calculation of dipole moment and polarizability

of low-lying excited states of Water, Ozone, Carbon mono-hydride cation and Hydrogen mono-fluoride are presented.

First static hyper-polarizabilities of few doublet radicals are presented in chapter 4. The implementation and the code development for this purpose has been described. Static hyper-polarizabilities of OH, OF, NO and NO₂, at the ground state are presented. Orbital-relaxed finite field FSMRCC values have been reported for comparison. In some cases, CVA-FSMRCC results have been compared with ROHF results.

In chapter 5, static hyper-polarizabilities of the first electronic excited states of closed shell molecules are presented. Calculations were done using CVA-FSMRCCSD method. The implementation and the code developed for this purpose have been discussed. Hyper-polarizabilities of the singlet and the triplet excited states of water, ozone and carbon mono-hydride cation are presented.

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Chapter 2

Dipole moment and static polarizability of open shell molecules and radicals

In this chapter, analytic dipole moments and dipole polarizabilities few open shell molecules e.g., hydroxyl radical, oxygen mono-fluoride, nitrogen monoxide and nitrogen dioxide are presented using constrained variational approach in Fock-space multi-reference coupled-cluster singles and doubles (CVA-FSMRCCSD) method. All of these molecules are important in atmospheric chemistry. The near-degeneracy in low-lying states of these molecules demands for multi-reference description of the wave-function. The study of variation in the properties of oxygen mono-fluoride with respect to the basis set is also presented.

2.1 Introduction

In chapter 1, multi-reference (MR) coupled-cluster (CC) methods [1–12] and Lagrangian based FSMRCC formalism [13–15] are described. Computational developments and first implementation of Lagrangian based FSMRCC for the calculation of dipole moment and polarizability of open shell molecules at the ground state was done by Manohar and Pal [14, 15]. In this chapter, few more application is done. More importantly, analytic FSMRCC results are compared with non-relaxed finite-field FSMRCC results to test the analytic FSMRCC code. Fock-space (FS) MRCC [1, 4, 5, 10–12] method is based on the concept of common vacuum. The choice of vacuum depends on the requirement of the study. In FSMRCC method, vacuum is not a physical vacuum. Usually, N electron RHF determinant of closed shell electronic configuration is taken as reference vacuum. Any system may be defined by the number of holes and particles present in the system with respect to this vacuum. A valence-universal wave-operator brings in the interactions of the model space configurations with the virtual space and thus introduces the commonly known dynamical electron correlation. In contrast, the HSMRCC [1, 6, 7, 16–18] method uses different vacuum for different configurations of the model-space; and a state-universal wave-operator is defined to incorporate the dynamical electron correlation. Due to the different inherent features, these methods differ in their domains of applicability. While FSMRCC is suitable for accounting the near-degeneracy in cases of ionized, electron attached and electronically excited states of molecules [13, 19, 20], HSMRCC is more appropriate for cases like bond-dissociation, potential energy surface, etc. [21–24] Both these methods suffer from the so-called intruder state problems [22, 25–28]. However, this problem can be easily eliminated by

proper choice of vacuum and active space. Both, FSMRCC and HSMRCC use the intermediate Hamiltonian [29, 30] formulation and multi-root in nature. Due to multi-root nature of the effective Hamiltonian, evaluation of energy derivatives in FSMRCC and HSMRCC frame-work are not trivial.

To calculate molecular properties, e.g. electric and magnetic properties, gradient, Hessians etc., energy derivatives with respect to field perturbation should be evaluated. The linear response technique within effective Hamiltonian [28, 30, 32] based MRCC methods was initiated by Pal [33] and applied by Pal and co-workers [34, 35], Hirao and co-workers [36] and Ajitha et al. [37] for obtaining analytical dipole moments of doublet radicals and electronic excited states. However, the method was quite unsatisfactory as it required time consuming evaluation of wave-function derivatives for every mode of perturbation. An attempt of introducing Z-vector technique in MRCC framework [38] was also made. However, a more satisfactory method, along the lines of single reference (SR) CC was only obtained after formulation of constrained variational response approach (CVA) in MRCC framework [39–41]. Szalay also formulated CVA in FSMRCC context [42] for complete model spaces only. The formulation of Shamasundar et al. [41] is, in general, applicable to incomplete model spaces. The first implementation of this method for analytical dipole moments and polarizabilities of some doublet radicals was done recently, by Manohar et. al. [14, 15] At present, the application of CVA-FSMRCC method is discussed for obtaining analytical dipole moments and polarizabilities of two important second row oxides, namely, oxygen mono-fluoride, nitric oxide and nitrogen dioxide. All these molecules are important in atmospheric chemistry. As far as polarizability is concerned, so far, there have been no theoretical results for these molecules and we present the first analytical polarizabilities of the molecules. For one-valence problem, the equations-of-motion coupled cluster (EOM-CC) [43–46] is indeed, equivalent to FSMRCC although; the equivalence breaks down for higher valence problems.

This chapter is organized as follows. In the next section, CVA-FSMRCC theory is discussed. Then, computational details is given. This is followed by the discussion of the results for analytic dipole moments and polarizabilities of OF, NO and NO₂ respectively.

2.2 CVA-FSMRCC theory for one valence system

The CVA formulation in FSMRCC framework is discussed in details in various articles [13–15, 19, 20, 41]. Here, we recapitulate the formulation very briefly and mention the CVA-FSMRCC working equations for ionized case. The equations for electron attached states are trivially obtained by reversal of hole-particle indices. The universal wave-operator Ω for one-hole problem is

$$\Omega = \{e^{T^{(0,0)}} e^{T^{(0,1)}}\} \quad (2.1)$$

Usual notations are used in the above equation and throughout this thesis. The wave-operator satisfies Bloch equation

$$\begin{aligned} P^{(0,1)}[H\Omega - \Omega H_{eff}^{(0,1)}]P^{(0,1)} &= 0 \\ &\text{and} \\ Q^{(0,1)}[H\Omega - \Omega H_{eff}^{(0,1)}]P^{(0,1)} &= 0 \end{aligned} \quad (2.2)$$

The effective Hamiltonian (H_{eff}) and Ω are obtained by solving the equations resulting after left projection of the above equation with model space and virtual space components respectively. The diagonalization of the effective Hamiltonian yields the roots, which are the energies of the corresponding exact states. As a result of normal ordering, subsystem embedding condition (SEC) holds due to which, one can systematically solve for the cluster amplitudes starting from the zero valence (0,0) sector of FS upwards upto the desired valence sector.

The energy of a specific state of the ionized system is given by

$$E_\mu = \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} (H_{eff})_{ij}^{(0,1)} C_{j\mu}^{(0,1)} \quad (2.3)$$

We construct the Lagrangian to minimize the energy expression given above, with the constraint that the MRCC equations are satisfied for the state μ .

$$\begin{aligned} \mathfrak{S} = & \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} (H_{eff})_{ij}^{(0,1)} C_{j\mu}^{(0,1)} \\ & + P^{(0,1)} \Lambda_2^{(0,1)} P^{(0,1)} P^{(0,1)} [H\Omega - \Omega H_{eff}^{(0,1)}] P^{(0,1)} \\ & + P^{(0,1)} \Lambda_1^{(0,1)} Q^{(0,1)} Q^{(0,1)} [H\Omega - \Omega H_{eff}^{(0,1)}] P^{(0,1)} \\ & + P^{(0,0)} \Lambda_2^{(0,0)} P^{(0,0)} P^{(0,0)} H\Omega P^{(0,0)} \\ & + P^{(0,0)} \Lambda_1^{(0,0)} Q^{(0,0)} Q^{(0,0)} H\Omega P^{(0,0)} \\ & - E_\mu \left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)} C_{j\mu}^{(0,1)} - 1 \right) \end{aligned} \quad (2.4)$$

The Λ -s in Eq. (2.4) are the Lagrange multipliers. However, in case of CMS, the effective Hamiltonian has an explicit expression in terms of cluster operators, as a result of which, the closed part in the Lagrange multiplier vanishes. The Eq. (2.4) thus reduces to

$$\begin{aligned} \mathfrak{S} = & \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} (H_{eff})_{ij}^{(0,1)} C_{j\mu}^{(0,1)} \\ & + P^{(0,1)} \Lambda^{(0,1)} Q^{(0,1)} Q^{(0,1)} [H\Omega - \Omega H_{eff}^{(0,1)}] P^{(0,1)} \\ & + P^{(0,0)} \Lambda^{(0,0)} Q^{(0,0)} Q^{(0,0)} H\Omega P^{(0,0)} \\ & - E_\mu \left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)} C_{j\mu}^{(0,1)} - 1 \right) \end{aligned} \quad (2.5)$$

Differentiation of Eq. (2.5) with respect to Λ results in expression for cluster amplitudes, i.e., the Bloch equation. It is obviously seen that the equations for Ω amplitudes are decoupled from the Λ amplitudes. However, evaluation of Λ requires Ω amplitudes. Λ amplitudes are calculated by making the Lagrangian stationary with respect to the cluster amplitudes. The Lagrangian defined in Eq. (2.5) can be differentiated with respect to

the field g to obtain the Lagrangians at every order. The zeroth-order and the first-order Lagrangians can therefore, be written as

$$\begin{aligned}
\mathfrak{S}^{(0)} = & \left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(0)} C^{(0,1)(0)} \right)_{\mu\mu} \\
& + P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(0)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{(0,1)(0)}] P^{(0,1)} \\
& + P^{(0,0)} \Lambda^{(0,0)(0)} [H^{(0)} \Omega^{(0)}] P^{(0,0)} \\
& - E_{\mu} \left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(0)} - 1 \right)
\end{aligned} \tag{2.6}$$

$$\begin{aligned}
\mathfrak{S}^{(1)} = & \left(\tilde{C}^{(0,1)(1)} H_{eff}^{(0,1)(0)} C^{(0,1)(0)} \right)_{\mu\mu} + \left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(1)} C^{(0,1)(0)} \right)_{\mu\mu} \\
& + \left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(0)} C^{(0,1)(1)} \right)_{\mu\mu} \\
& + P^{(0,1)} \Lambda^{(0,1)(1)} [H^{(0)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{(0,1)(0)}] P^{(0,1)} \\
& + P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(1)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{(0,1)(1)}] P^{(0,1)} \\
& + P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(0)} \Omega^{(1)} - \Omega^{(1)} H_{eff}^{(0,1)(0)}] P^{(0,1)} \\
& + P^{(0,0)} \Lambda^{(0,0)(1)} H^{(0)} \Omega^{(0)} P^{(0,0)} + P^{(0,0)} \Lambda^{(0,0)(0)} H^{(1)} \Omega^{(0)} P^{(0,0)} \\
& + P^{(0,0)} \Lambda^{(0,0)(0)} H^{(0)} \Omega^{(1)} P^{(0,0)} \\
& - E_{\mu}^{(0)} \sum_{ij} \left(\tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(1)} + \tilde{C}_{\mu i}^{(0,1)(1)} C_{j\mu}^{(0,1)(0)} \right) \\
& - E_{\mu}^{(1)} \left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(0)} - 1 \right)
\end{aligned} \tag{2.7}$$

The Eq.s (2.6) and (2.7) give the energy and the first order energy derivative for the state μ . Because of stationarity of Lagrangian with respect to Λ and Ω , the above expressions are further simplified. The energy derivatives follow $(2n + 1)$ rule with respect to the Ω amplitudes and $(2n + 2)$ rule with respect to Λ amplitudes. There is a $(2n + 1)$ rule for the eigen-vectors $\tilde{C}^{(0,1)}$ and $C^{(0,1)}$ for evaluation of energy derivatives. With these, the expressions for Lagrangians given in Eqs. (2.6) and (2.7) simplify. We

denote this simplified Lagrangian as \mathfrak{S}_{opt} .

$$\mathfrak{S}_{opt}^{(0)} = \left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(0)} C^{(0,1)(0)} \right)_{\mu\mu} \quad (2.8)$$

$$\begin{aligned} \mathfrak{S}_{opt}^{(1)} &= \left[\tilde{C}^{(0,1)(0)} H_{eff\Omega^{(0)}}^{(0,1)(1)} C^{(0,1)(0)} \right]_{\mu\mu} \\ &+ P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(1)} \Omega^{(0)} - \Omega^{(0)} H_{eff\Omega^{(0)}}^{(0,1)(1)}] P^{(0,1)} \\ &+ P^{(0,0)} \Lambda^{(0,0)(0)} H^{(1)} \Omega^{(0)} P^{(0,0)} \end{aligned} \quad (2.9)$$

$$\begin{aligned} \mathfrak{S}_{opt}^{(2)} &= \left[\tilde{C}^{(0,1)(0)} H_{eff\Omega^{(1)}}^{(0,1)(2)} C^{(0,1)(0)} \right]_{\mu\mu} \\ &+ P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(2)}] P^{(0,1)} \\ &+ P^{(0,0)} \Lambda^{(0,0)(0)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)}] P^{(0,0)} \\ &+ 2 \left(\left[\tilde{C}^{(0,1)(1)} H_{eff}^{(0,1)(0)} C^{(0,1)(1)} \right]_{\mu\mu} - E_{\mu}^{(0)} \sum_i \tilde{C}^{(0,1)(1)} C^{(0,1)(1)} \right) \end{aligned} \quad (2.10)$$

The subscript $\Omega^{(0)}$ indicates that the derivative effective Hamiltonian does not contain any term formed from derivatives of the cluster amplitudes. The first order properties can thus be obtained simply with the knowledge of Ω and Λ amplitudes only. The subscript $\Omega^{(1)}$ in Eq. (2.10) indicates that only first derivative of Ω is used. As mentioned earlier, for polarizability, which is second order energy derivative, requires first derivative of Ω , but, not for Λ . Differentiation of Eq. (2.6) with respect to Λ amplitudes leads the equations for Ω amplitudes – the Bloch equations. The Λ are obtained by differentiating Eq. (2.6) with respect to Ω amplitudes. It may be noticed that the coupling within the Λ amplitudes in various valence sectors is exactly opposite of SEC. Thus, one has to solve for the Λ amplitudes successively from the highest valence sector to the lowest valence sector. The CVA method is a single-root method. The Λ amplitudes depend on the desired state of the molecule. Therefore, for every state one has to calculate the Λ amplitudes separately. In contrast, the non-variational response of FSMRCC [37] has a multiple-root structure. However, the expensive evaluation of wave-function derivatives

for each mode of perturbation is avoided in CVA-FSMRCC. Also, the single-root feature makes CVA more attractive for the cases like curve-crossing studies of excited states, etc. than the non-variational response method. It can be seen that the Λ equations for one-valence problem are same as the "zeta equations" in the EOMCC method [43–46].

The Λ equations contain a few disconnected terms which might affect the size-extensivity. However, these terms are perturbatively less important. In spite of these problems, the higher order properties are accurately evaluated with the knowledge of lower order amplitudes.

2.3 Computational details

The universal wave operator Ω in case of the ionized states is $[e^{T^{(0,0)}} e^{T^{(0,1)}}]$, whereas for the electron attached radicals, it is $[e^{T^{(0,0)}} e^{T^{(1,0)}}]$. The $T^{(0,0)}$ equations are decoupled from the valence sector T equations due to SEC. Using this advantageous fact, we first solve for the $(0, 0)$ sector amplitudes. Before solving for the valence sector cluster amplitudes, store the $[\hat{H}e^{(T^{(0,0)})}]_C$, which is called \bar{H} . The closed part of \bar{H} , i.e. $(\bar{H})_{cl}$ is the ground state energy. If this part is omitted during the solution of the $(0, 1)$ and $(1, 0)$ sector cluster amplitudes ionization potentials and electron affinities are obtained directly. The open parts of \bar{H} can further be divided into one body, two body, three body parts and so on. Under the SD approximation, only upto three body parts contribute to the valence sector cluster equations as well as to the Λ equations for these sectors. Because of the large dimensions, the three body parts of the \bar{H} can not be stored in the hard disk. These are, therefore, evaluated in the code as and when required. The one and two-body parts of \bar{H} are calculated only once and are saved in memory or hard-disk.

The equations for Λ amplitudes are inhomogeneous linear simultaneous equations and as explained earlier, the Λ amplitudes of the valence sector are first obtained

followed by solution of the Λ amplitudes of the $(0, 0)$ sector. The Jacobi's iterative procedure has been used for obtaining the Λ amplitudes. To test the analytic code, non-relaxed finite-field FSMRCC results are compared with analytic FSMRCC results. For non-relaxed finite-field calculation, field perturbation is introduced after SCF level. Thus, orbitals used for different field values are same. For relaxed finite-field calculation, field perturbation is used in the SCF level. Finite-field dipole moment is calculated as the first derivative of energy and polarizability as the second derivative of energy using three point and five point formula respectively. Field value used for both relaxed and non-relaxed finite-field calculations are in steps of ± 0.001 a.u.

2.4 Results and Discussion

In this section, results for analytic dipole moments and dipole polarizabilities of hydroxyl radical, oxygen mono-fluoride, nitric oxide and nitrogen dioxide are discussed using CVA-FSMRCCSD method. To test the analytic code, dipole moment and polarizability values of hydroxyl radical and nitric oxide are compared with non-relaxed finite-field FSMRCC results. For comparison of analytic results with other theoretical results, ROHF, FCI and relaxed finite-field dipole moment results are presented for OF molecule. For OF molecule, both dipole moments and polarizabilities are calculated for four different basis sets. For nitric oxide and nitrogen dioxide, analytic results are compared with relaxed finite-field FSMRCC results. Experimental dipole moment values are reported for OF, NO and NO₂.

2.4.1 Validation of analytic code

One valence problem in Fock-space may be treated as one-hole problem $[(0,1)$ sector] or one-particle problem $[(1,0)$ sector]. To test $(0,1)$ sector code, OH radical is taken

as test example, while, for (1,0) sector code, NO is chosen as test molecule. Calculated results are presented in Table 2.1.

Table 2.1: Dipole moments and polarizabilities of OH and NO. Z-axis is molecular axis. Comparison with non-relaxed finite-field FSMRCC results.

Molecule	Basis	property	analytic FSMRCCSD	finite-field FSMRCCSD
OH	aug-cc-pVDZ	dipole moment	0.617140	0.617139
		polarizability	10.390250	10.390525
	Sadlej-pVTZ	dipole moment	0.637491	0.637496
		polarizability	10.995285	10.995281
NO	aug-cc-pVDZ	dipole moment	0.071396	0.071394
		polarizability	14.314714	14.314710
	Sadlej-pVTZ	dipole moment	0.073918	0.073917
		polarizability	14.656719	14.656722

All results are in atomic units.

OH radical may be treated as one-hole problem with respect to the RHF determinant of $\text{OH}^{(-)}$ as vacuum. Two-fold degenerate HOMO of $\text{OH}^{(-)}$ radical is chosen as active holes. O-H bond length is 1.85140 a.u. For NO molecule, RHF determinant of $\text{NO}^{(+)}$ is chosen as reference vacuum and two-fold degenerate LUMO orbitals are chosen as active particles. N-O bond distance is taken as 2.155 a.u. aug-cc-pVDZ and Sadlej-pVTZ [47] basis are used for calculation of both OH radical and NO molecule. For all cases, analytic

dipole moments and polarizabilities agree with non-relaxed FSMRCC values up to 6th digit after decimal point. This serves as the validation of analytic codes.

2.4.2 Oxygen monofluoride

Oxygen mono fluoride radical can be viewed as ionized state of oxygen mono fluoride anion resulting from removal of an electron from the HOMO, which has π character. The ground state of the radical is thus a π -type doublet represented by $^2\pi$. Thus, for FSMRCC calculations, we start with the RHF of oxygen mono fluoride anion as vacuum with respect to which the low-lying states of OF radical are one hole problem. The active orbitals are the two fold degenerate HOMO of OF⁻ radicals. Thus we described the ground $^2\pi$ state of OF radical. The ground state geometry of OF radical (Req=2.5953 a.u.) [48] was used. Thus in the FSMRCC frame work we solve for the (0,0) and (0,1) sector cluster amplitudes respectively, followed by Λ amplitudes in the reverse order. We have done an extensive study on the basis set dependence of the properties of this system by choosing STO-3G, cc-pVDZ, aug-cc-pVDZ and Sadlej-pVTZ as basis. The ground state dipole moment of oxygen mono fluoride radical are given in Table 2.2. Experimental dipole moment, 0.0017 a.u. [48], is extremely small. However, ROHF values of the dipole moment of ground state of OF radical in most of the basis, except STO-3G, are quite large, greater than 0.2 a.u. This indicates the importance of electron correlation effects. ROHF dipole moments are far away from the experimental value except in the case of STO-3G basis. We see that the correlation effects are recovered quite well in the basis sets used, so that the net results are closed to the experimental value. The STO-3G calculation, however produces a very low value of ROHF dipole moment for this state and the correlation correction to the dipole is, in fact, opposite to those in the other basis sets. Only for this basis, Full CI calculation could be performed and thus the CVA-FSMRCCSD value was compared with this. We observe the trend of Full CI also

Table 2.2: Dipole moment of OF molecule in different basis sets. Z-axis is molecular axis.

Basis	analytic FSMRCCSD	finite-field FSMRCCSD	ROHF	Full CI
STO-3G	0.1391	0.1461	0.0214	0.0892
cc-pVDZ	0.0133	0.0100	0.2275	0.0393
aug-cc-pVDZ	0.0084	0.0054	0.2082	
Sadlej-pVTZ	0.0004	0.0062	0.2062	

experimental value is 0.0017

All results are in atomic units.

is the same as that obtained by the present method.

In addition we have calculated dipole polarizability along molecular axis (α_{zz}) and perpendicular to molecular axis (α_{xx}) and (α_{yy}) using cc-pVDZ, aug-cc-pVDZ and Sadlej-pVTZ basis sets. Results are given in Table 2.3. Polarizability values generally increase with basis. There are no benchmark results to compare with. However these have been compared with finite field values. A general agreement is observed.

2.4.3 Nitric oxide

NO molecule may be treated as electron attached state of NO^+ with respect to which NO molecule may be considered as one particle problem of FSMRCC. Two-fold degenerate LUMO (π) orbitals was chosen as active particles. Addition of one electron in one of the active orbitals results in the formation of the corresponding radical. $^2\Pi$ state of NO molecule have been reported in two different basis sets; aug-cc-pVDZ and Sadlej-pVTZ. N-O bond distance has been used for this calculation is 2.15501 a.u. Calculated

Table 2.3: Polarizability of OF molecule in different basis sets. Z-axis is molecular axis.

Basis	component of polarizability	analytic FSMRCCSD	finite-field FSMRCCSD
STO-3G	α_{zz}	6.42	5.22
	$\alpha_{xx}=\alpha_{yy}$	0.15	1.16
cc-pVDZ	α_{zz}	11.56	8.79
	$\alpha_{xx}=\alpha_{yy}$	2.56	2.79
aug-cc-pVDZ	α_{zz}	15.74	13.32
	$\alpha_{xx}=\alpha_{yy}$	7.55	6.70
Sadlej-pVTZ	α_{zz}	16.57	15.07
	$\alpha_{xx}=\alpha_{yy}$	9.76	7.54

All results are in atomic units.

results have been presented in Table 2.4. Experimental dipole moment of NO [49] is also presented for comparison.

Analytic value of dipole moment for both the bases are closer to the experimental value. Analytic and finite-field dipole moment values are opposite side of experimental value. It is also found that, difference of dipole moment values between finite-field value and experimental value is larger than the difference between analytic value and experimental value. The orbital relaxation effect is more for the Sadlej-pVTZ basis than aug-cc-pVDZ basis. The polarizability of NO molecule along molecular axis is presented

Table 2.4: Dipole moments and polarizabilities of NO. Z-axis is molecular axis.

Basis	property	analytic FSMRCCSD	finite-field FSMRCCSD
aug-cc-pVDZ	dipole moment	0.0714	0.0519
	polarizability	14.32	14.49
Sadlej-pVTZ	dipole moment	0.0739	0.0432
	polarizability	14.66	17.10

experimental dipole moment is 0.0628

All results are in atomic units.

here. Analytic polarizability values for both the basis are closer to each other. Finite-field polarizability for aug-cc-pVDZ basis is closer to analytic value which is not true for Sadlej-pVTZ basis. This may be due to the larger orbital relaxation effect for this basis.

2.4.4 Nitrogen di-oxide

Nitrogen di-oxide may be considered as electron attached state of Nitrogen dioxide cation. RHF configuration of Nitrogen di-oxide cation was taken as vacuum in this case for CVA-FSMRCCSD calculation. Thus Nitrogen di-oxide radical is considered as one particle system. We have the first two unoccupied orbitals as active. The FSMRCC produces two low-lying states of NO_2 . However, we have done the calculation with the ground state geometry. Hence, only the values of the ground state have been reported. For dipole moment calculation, we start with cluster amplitudes for (0,0) sector first and

then for (1,0) sector, followed by solution of Λ equations in the reverse order. Derivative of cluster amplitudes were also done for polarizability calculation which forced us to evaluate Λ vectors. Λ amplitudes as explained earlier were calculated in the reverse order of SEC. Dipole moment and polarizabilities of Nitrogen di-oxide calculated in cc-pVDZ and DZP+sp diffuse basis set are given in Table 2.5. N-O bond length is 2.26276 a.u. and O-N-O bond angle is 133.8° [50]. CVA-FSMRCCSD dipole moment is 0.138

Table 2.5: Dipole moments and polarizabilities of NO_2 molecule. Z-axis is molecular axis.

State	method	μ_z	α_{zz}	α_{xx}	α_{yy}
2A_1	analytic FSMRCCSD	0.1377	8.08	24.20	5.77
	finite-field FSMRCCSD	0.1757	8.20	23.84	4.97
experimental dipole moment is 0.114					

All results are in atomic units.

a.u. is higher than experimental value 0.114 a.u. [51] but better than FF-FSMRCCSD which is 0.176 a.u. As Nitrogen di-oxide is a planar molecule we do expect non-zero value of polarizability for all three directions. Among three polarizability values polarizability perpendicular to molecular axis i.e. (α_{xx}) is largest. Polarizability perpendicular to the molecular plane (α_{yy}) is very small as expected. CVA-FSMRCCSD values are comparable to FF-FSMRCCSD value in each and every case.

2.5 Conclusion

In this chapter, we have presented analytical dipole moment and polarizability of Oxygen mono fluoride and Nitrogen di-oxide using CVA-FSMRCCSD method. These molecules can be described by (0,1) and (1,0) Fock space sectors, respectively. The method involving two sets of amplitudes, one normal Fock-space amplitudes and the other amplitudes of Λ -operator, having a structure conjugate to the Fock-space cluster operators. We observe that the method provides an efficient tool to obtain higher order properties with the knowledge of lower order cluster amplitudes. We have also found that for any system, where electron correlation has a major contribution, like oxygen mono fluoride, we need larger basis calculation to take care of electron correlation in a proper way for calculation of molecular properties.

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Chapter 3

Excited state dipole moment and polarizability of closed shell molecules

In this chapter, implementation of CVA-FSMRCC method for the low-lying electronic excited states of closed shell molecules are discussed. In particular, dipole moment and polarizability of water, ozone, hydrogen mono-fluoride and carbon mono hydride cation are presented along with theoretical discussion. Comparison of CVA-FSMRCC method with EOM-CC method for the first excited states is studied for water and ozone molecule. Basis set convergence is also studied for CH^+ molecule.

3.1 Introduction

In chapter 1 and 2, importance of single reference coupled cluster (SRCC) methods [1–11] and multi-reference coupled cluster (MRCC) methods [12–37] are described. In chapter 2, Lagrangian based linear response approach which is termed as constrained variational approach (CVA) to Fock space Multi-reference coupled cluster (FSMRCC) [32, 34–37] is described for one valence problem in Fock space to calculate electric dipole moment and dipole polarizability at the ground state. In this chapter, CVA-FSMRCC method is implemented for the first electronic excited states of the closed shell molecules. Implementation is done for the calculation of few low-lying excited states of water, ozone, hydrogen mono-fluoride and carbon mono-hydride cation. In some cases, ground state geometries and for some other cases excited state geometries are used. Comparison of analytic results with non-relaxed FSMRCC is done for CH^+ molecule. For water, ozone and HF molecule CVA-FSMRCC results are compared with relaxed finite-field and Equation of motion coupled cluster (EOM-CC) [38–54] results. The nonequivalence of CVA-FSMRCC and EOM-CC for the two valence problem is reflected from these comparison which is stated in chapter 2. The basis set convergence is also studied for CH^+ molecule. The use of ground state geometry and the specific excited state geometries for the calculation of dipole moments and polarizabilities of the singlet and the triplet B_1 excited states of water shows the effect of geometric relaxation.

3.2 Effective Hamiltonian for excited states

In this section, we briefly mention the FSMRCC algebra in the context of one-particle one-hole case. For a pedagogical description, readers may refer to other articles. [19, 23, 25, 26] As is known, (1, 1) FS sector problem is a special type of IMS, often called quasi-complete model space (QMS). Here it should be mentioned that ϕ_{HF} is

outside the model space. The universal wave operator for EE problem is

$$\Omega = \{e^{T^{(0,0)}} e^{T^{(0,1)}} e^{T^{(1,0)}} e^{T^{(1,1)}}\} \quad (3.1)$$

Under singles and doubles (SD) approximation, the T operator of every sector will contain only one-body and two-body cluster operators. Following Mukherjee [19, 25], Sinha *et. al.* [23] and Pal *et. al.* [24] the above valence universal cluster operator satisfies Bloch equation.

$$H\Omega P^{k,l} = \Omega \tilde{H}_{eff}^{k,l} P^{k,l}; \forall k, l = 0, 1 \quad (3.2)$$

where, $\tilde{H}_{eff}^{(1,1)}$ includes contributions from the effective Hamiltonians of lower sectors in addition to the (1, 1) sector part, i.e. $H_{eff}^{(1,1)}$. For example, if μ and ν are indices for active holes and α and β are active particle indices, then the matrix elements of $\tilde{H}_{eff}^{(1,1)}$ can be written as

$$(\tilde{H}_{eff})_{\mu\alpha,\nu\beta}^{(1,1)} = (H_{eff})_{\mu\alpha,\nu\beta}^{(1,1)} + (H_{eff})_{\mu,\nu}^{(0,1)} \delta_{\alpha,\beta} + (H_{eff})_{\alpha,\beta}^{(1,0)} \delta_{\mu,\nu} + H_{eff}^{(0,0)} \quad (3.3)$$

The cluster amplitudes and the effective Hamiltonian for the EE problem are obtained by solving the following projected Bloch equations.

$$P^{(k,l)} H\Omega - \Omega \tilde{H}_{eff} P^{(k,l)} = 0; \forall k, l = 0, 1 \quad (3.4)$$

$$Q^{(k,l)} H\Omega - \Omega \tilde{H}_{eff} P^{(k,l)} = 0; \forall k, l = 0, 1 \quad (3.5)$$

The normal ordering in the ansatz leads to SEC resulting in decoupling of lower valence sector equations from the higher ones. It was shown by Mukherjee [19] that for the above IMS, the linked nature of effective Hamiltonian and the cluster operators can be ensured if one abandons the requirement of intermediate normalization, i.e.

$$P^{(1,1)} \Omega P^{(1,1)} \neq P^{(1,1)} \quad (3.6)$$

Applying Wick's theorem [55–57] on Eq. (3.4) and simplifying, one can write

$$P^{(k,1)} \widehat{H\Omega} P^{(k,l)} = P^{(k,l)} (\widehat{\Omega^{(k,l)} \tilde{H}_{eff}^{(k,l)}} P^{(k,l)} + P^{(k,l)} [\tilde{\Omega}^{(k,l)} - \widehat{\Omega^{(k,l)}}] H_{eff} P^{(k,l)} \quad (3.7)$$

where the cap over two operators indicates contraction. In the above equation, the $\tilde{\Omega}^{(k,l)}$ subsumes the lower valence cluster operators. For CMS, there are vanishing $P - P$ projector for the composites $\widehat{\tilde{\Omega}^{(k,l)}\tilde{H}_{eff}}$ or $\widehat{\tilde{\Omega}^{(k,l)}H_{eff}}$. For $(1, 1)$ sector problem, the non-vanishing terms could appear only through the product of $T_1^{(1,1)}$ and $T_1^{(0,0)}$ operators. However, $T_1^{(1,1)}$ contains only hole-particle destruction operators while $T_1^{(0,0)}$ contains only hole-particle creation operators, due to which, no connected component is possible using these operators. Thus, no non-vanishing $P - P$ projector as discussed above is possible in this case leading to simplification similar to the case, where intermediate normalization is valid (like in CMS). We can thus, construct the effective Hamiltonian over the model space as

$$P^{(1,1)}\tilde{H}_{eff}^{(1,1)}P^{(1,1)} = P^{(1,1)}H\Omega P^{(1,1)} \quad (3.8)$$

The equations of all the cluster amplitudes ($T_2^{(1,1)}$ and one and two-body cluster operators of lower valence sectors in the present case) as well as the effective Hamiltonian are independent of $T_1^{(1,1)}$. Although the FSMRCCSD wave function consists of $T_1^{(1,1)}$ amplitudes, these do not couple with higher body cluster operators, effective Hamiltonian as well as the corresponding derivative equations. Thus, under SD approximation, we have effectively, only two-body cluster amplitudes of $(1, 1)$ sector. Therefore, we denote the $(1, 1)$ sector cluster operator as $T^{(1,1)}$ rather than $T_2^{(1,1)}$ for convenience. Similar strategy will also be used for the Lagrange multipliers of this sector. Due to spin adaptation, two different types of $H_{eff}^{(1,1)}$, $T^{(1,1)}$ and $\Lambda^{(1,1)}$ exist. They are indicated as $(H_{eff}^A)^{(1,1)}$ and $(H_{eff}^B)^{(1,1)}$, $T^{A(1,1)}$ and $T^{B(1,1)}$, $\Lambda^{A(1,1)}$ and $\Lambda^{B(1,1)}$ respectively. $(H_{eff}^A)^{(1,1)}$, $(H_{eff}^B)^{(1,1)}$, $T^{A(1,1)}$ and $T^{B(1,1)}$ are shown in Figure 3.1.

The equations for $(H_{eff}^A)^{(1,1)}$ and $T^{A(1,1)}$ are completely decoupled from the equations of the type- B quantities. However, the type- B quantities depend on the quantities of type- A . Thus in addition to SEC, there is further decoupling of type- A block from the

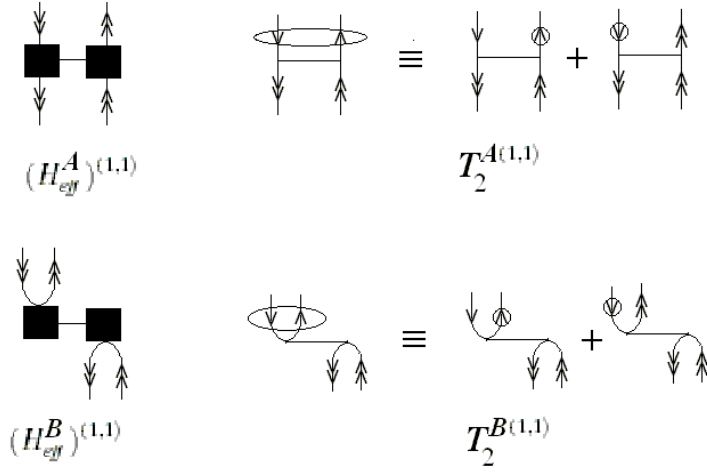


Figure 3.1: Effective Hamiltonian and $T_2^{(1,1)}$ diagrams after spin adaptation

type-*B* one. After spin adaptation, effective Hamiltonians for singlet and triplet excited states are obtained, the matrix elements of which, can be written as

$$\begin{aligned}
 (H_{eff}^{singlet})_{\mu\alpha,\nu\beta}^{(1,1)} &= (H_{eff}^A)_{\mu\alpha,\nu\beta}^{(1,1)} - 2(H_{eff}^B)_{\mu\alpha,\nu\beta}^{(1,1)} \\
 &\quad + (H_{eff})_{\mu,\nu}^{(0,1)} \delta_{\alpha,\beta} + (H_{eff})_{\alpha,\beta}^{(1,0)} \delta_{\mu,\nu} + H_{eff}^{(0,0)}
 \end{aligned} \tag{3.9}$$

and

$$\begin{aligned}
 (H_{eff}^{triplet})_{\mu\alpha,\nu\beta}^{(1,1)} &= (H_{eff}^A)_{\mu\alpha,\nu\beta}^{(1,1)} \\
 &\quad + (H_{eff})_{\mu,\nu}^{(0,1)} \delta_{\alpha,\beta} + (H_{eff})_{\alpha,\beta}^{(1,0)} \delta_{\mu,\nu} + H_{eff}^{(0,0)}
 \end{aligned} \tag{3.10}$$

where, the indices $\{\mu, \nu, \alpha, \beta\}$ are as defined in Eq. (3.3)

The triplet excited states can thus be obtained by simply solving up to the type-*A* Bloch equations. The singlet states calculation is, however, relatively more complicated as it requires the knowledge of both the types of quantities. If the $H_{eff}^{(0,0)}$ contribution is dropped, one can directly obtain excitation energies of the corresponding states.

3.3 CVA-FSMRCCSD ansatz for excited states

Constrained variational approach to FSMRCC was done by Shamasundar *et al.* [32] The general expression for the first and second derivatives for both one valence and two valence problem were given in the appendix of the reference mentioned above. The Lagrangian for energy and expression for first and second order properties of triplet excited state have been presented previously by Manohar and Pal, [35] but for convenience we write them in this paper for both singlet and triplet states. Property calculation by constructing such Lagrangian has been implemented so far in a completely orbital non relaxed approach. The construction of Lagrangian for electronic structure calculation of specific excited state depends on the spin multiplicity of the state. As seen in the previous section, the triplet excited states are completely independent of direct types. Energy of a m -th excited singlet state of a system is given by

$$E_m^{singlet} = \sum_{ij} \tilde{C}_{mi}^{singlet(1,1)} (H_{eff}^{singlet})_{ij}^{(1,1)} C_{jm}^{singlet(1,1)} \quad (3.11)$$

We construct Lagrangian for this state as

$$\begin{aligned} \mathfrak{S}^{singlet} = & \sum_{ij} \tilde{C}_{mi}^{singlet(1,1)} (H_{eff}^{singlet})_{ij}^{(1,1)} C_{jm}^{singlet(1,1)} \\ & + P^{(1,1)} \Lambda^{B(1,1)} [H\Omega - \Omega H_{eff}^{singlet(1,1)}]_B P^{(1,1)} \\ & + P^{(1,1)} \Lambda^{A(1,1)} [H\Omega - \Omega H_{eff}^{singlet(1,1)}]_A P^{(1,1)} \\ & + P^{(0,1)} \Lambda^{(0,1)} [H\Omega - \Omega H_{eff}^{(0,1)}] P^{(0,1)} \\ & + P^{(1,0)} \Lambda^{(1,0)} [H\Omega - \Omega H_{eff}^{(1,0)}] P^{(1,0)} \\ & + P^{(0,0)} \Lambda^{(0,0)} [H\Omega - \Omega H_{eff}^{(0,0)}] P^{(0,0)} \\ & - E_m^{singlet} \left(\sum_{ij} \tilde{C}_{mi}^{singlet(1,1)} C_{jm}^{singlet(1,1)} - 1 \right) \end{aligned} \quad (3.12)$$

The Λ vectors and cluster amplitudes are obtained by making the Lagrangian stationary with respect to cluster amplitudes and Λ vectors respectively. The eigen vectors are also

obtained variationally. The cluster amplitudes are thus completely decoupled from the Λ vectors. As discussed by Pal and co-workers, [32, 34] there is a reverse SEC decoupling scheme for the Λ vectors of various sector. Moreover, the decoupling scheme between type- A and type- B $\Lambda^{(1,1)}$ vectors is exactly in reverse order of $T^{(1,1)}$ amplitudes. Thus, for singlet state calculations, one has to solve for T -amplitudes from $(0, 0)$ -sector and upwards to $(1, 1)'B'$ -sector, followed by solution of $\Lambda^{B(1,1)}$, then $\Lambda^{A(1,1)}$ and so on up to vacuum sector, i.e. $\Lambda^{(0,0)}$.

For triplet state calculations, it is necessary to construct Lagrangian using triplet state effective Hamiltonian. Since, the triplet states are independent of type- B quantities, the Lagrangian for a specific triplet state will contain only type- A quantities.

Triplet states are obtained by diagonalization of triplet state effective Hamiltonian. Thus m -th triplet excited state is given by

$$E_m^{triplet} = \sum_{ij} \tilde{C}_{mi}^{triplet(1,1)} (H_{eff}^{triplet})_{ij}^{(1,1)} C_{jm}^{triplet(1,1)} \quad (3.13)$$

Similarly, for a specific singlet state, we can construct the Lagrangian for the above triplet state as follows.

$$\begin{aligned} \mathfrak{S}^{triplet} = & \sum_{ij} \tilde{C}_{mi}^{triplet(1,1)} (H_{eff}^{triplet})_{ij}^{(1,1)} C_{jm}^{triplet(1,1)} \\ & + P^{(1,1)} \Lambda^{A(1,1)} [H\Omega - \Omega H_{eff}^{triplet(1,1)}] P^{(1,1)} \\ & + P^{(0,1)} \Lambda^{(0,1)} [H\Omega - \Omega H_{eff}^{(0,1)}] P^{(0,1)} \\ & + P^{(1,0)} \Lambda^{(1,0)} [H\Omega - \Omega H_{eff}^{(1,0)}] P^{(1,0)} \\ & + P^{(0,0)} \Lambda^{(0,0)} [H\Omega - \Omega H_{eff}^{(0,0)}] P^{(0,0)} \\ & - E_m^{triplet} \left(\sum_{ij} \tilde{C}_{mi}^{triplet(1,1)} C_{jm}^{triplet(1,1)} - 1 \right) \end{aligned} \quad (3.14)$$

It may be noted that $\Lambda^{A(1,1)}$ vectors in Eq. (3.14) are different from the $\Lambda^{A(1,1)}$ vectors in Eq. (3.12), as there is no coupling with type- B quantities in Eq. (3.14). For energy

derivatives, the cluster amplitudes and eigen-vectors follow $(2n + 1)$ -rule, whereas, the Λ -vectors follow $(2n + 2)$ -rule.

The Λ equations of various sectors for triplet-state calculations are relatively simpler than the ones for the corresponding singlet states. We have developed the code for computing both singlet and triplet excited states of molecules with closed-shell ground state. We therefore, present the simplified expressions for first and second order properties (after application of the $(2n + 1)$ and $(2n + 2)$ rules) for singlet and triplet states.

$$\begin{aligned}
\mathfrak{S}_{opt}^{singlet(1)} &= \left(\tilde{C}^{singlet(1,1)(0)} H_{eff}^{singlet(1,1)(1)} \right)_{\Omega^{(0)}} C^{singlet(1,1)(0)} \Bigg)_{m,m} \\
&+ P^{(1,1)} \Lambda^{B(1,1)} [H^{(1)} \Omega - \Omega H_{eff}^{singlet(1,1)(1)}]_{\Omega^{(0)}}^B P^{(1,1)} \\
&+ P^{(1,1)} \Lambda^{A(1,1)} [H^{(1)} \Omega - \Omega H_{eff}^{triplet(1,1)(1)}]_{\Omega^{(0)}}^A P^{(1,1)} \\
&+ P^{(0,1)} \Lambda^{(0,1)} [H^{(1)} \Omega - \Omega H_{eff}^{(0,1)(1)}]_{\Omega^{(0)}} P^{(0,1)} \\
&+ P^{(1,0)} \Lambda^{(1,0)} [H^{(1)} \Omega - \Omega H_{eff}^{(1,0)(1)}]_{\Omega^{(0)}} P^{(1,0)} \\
&+ P^{(0,0)} \Lambda^{(0,0)} H^{(1)} \Omega P^{(0,0)}
\end{aligned} \tag{3.15}$$

$$\begin{aligned}
\mathfrak{S}_{opt}^{triplet(1)} &= \left(\tilde{C}^{triplet(1,1)(0)} H_{eff}^{triplet(1,1)(1)} \right)_{\Omega^{(0)}} C^{triplet(1,1)(0)} \Bigg)_{m,m} \\
&+ P^{(1,1)} \Lambda^{A(1,1)} [H^{(1)} \Omega - \Omega H_{eff}^{triplet(1,1)(1)}]_{\Omega^{(0)}}^A P^{(1,1)} \\
&+ P^{(0,1)} \Lambda^{(0,1)} [H^{(1)} \Omega - \Omega H_{eff}^{(0,1)(1)}]_{\Omega^{(0)}} P^{(0,1)} \\
&+ P^{(1,0)} \Lambda^{(1,0)} [H^{(1)} \Omega - \Omega H_{eff}^{(1,0)(1)}]_{\Omega^{(0)}} P^{(1,0)} \\
&+ P^{(0,0)} \Lambda^{(0,0)} H^{(1)} \Omega P^{(0,0)}
\end{aligned} \tag{3.16}$$

$$\begin{aligned}
\mathfrak{S}_{opt}^{singlet(2)} &= \left(\tilde{C}^{singlet(1,1)(0)} H_{eff}^{singlet(1,1)(2)} \right)_{\Omega^{(1)}} C^{singlet(1,1)(0)} \Big)_{m,m} \\
&+ P^{(1,1)} \Lambda^{B(1,1)(0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{singlet(1,1)})_{\Omega^{(1)}}^{(2)}] P^{(1,1)} \\
&+ P^{(1,1)} \Lambda^{A(1,1)(0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{triplet(1,1)})_{\Omega^{(1)}}^{(2)}] P^{(1,1)} \\
&+ P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(2)}] P^{(0,1)} \\
&+ P^{(1,0)} \Lambda^{(1,0)(0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{(1,0)})_{\Omega^{(1)}}^{(2)}] P^{(1,0)} \\
&+ P^{(0,0)} \Lambda^{(0,0)(0)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)}] P^{(0,0)} \\
&+ 2 \sum_{ij} \tilde{C}_{mi}^{singlet(1,1)(1)} H_{eff}^{singlet(1,1)(0)} C_{jm}^{singlet(1,1)(1)} \\
&- 2 E_m^{(0)} \sum_i \tilde{C}_{mi}^{singlet(1,1)(1)} C_{im}^{singlet(1,1)(1)} \tag{3.17}
\end{aligned}$$

$$\begin{aligned}
\mathfrak{S}_{opt}^{triplet(2)} &= \left(\tilde{C}^{triplet(1,1)(0)} H_{eff}^{triplet(1,1)(2)} \right)_{\Omega^{(1)}} C^{triplet(1,1)(0)} \Big)_{m,m} \\
&+ P^{(1,1)} \Lambda^{A(1,1)(0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{triplet(1,1)})_{\Omega^{(1)}}^{(2)}] P^{(1,1)} \\
&+ P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(2)}] P^{(0,1)} \\
&+ P^{(1,0)} \Lambda^{(1,0)(0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{(1,0)})_{\Omega^{(1)}}^{(2)}] P^{(1,0)} \\
&+ P^{(0,0)} \Lambda^{(0,0)(0)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)}] P^{(0,0)} \\
&+ 2 \sum_{ij} \tilde{C}_{mi}^{triplet(1,1)(1)} H_{eff}^{triplet(1,1)(0)} C_{jm}^{triplet(1,1)(1)} \\
&- 2 E_m^{(0)} \sum_i \tilde{C}_{mi}^{triplet(1,1)(1)} C_{im}^{triplet(1,1)(1)} \tag{3.18}
\end{aligned}$$

The subscripts $\Omega^{(0)}$ and $\Omega^{(1)}$ indicate that the corresponding terms are formed using up to zeroth and first order derivatives of the cluster amplitudes respectively. The first order properties can thus be obtained without the cumbersome solution of the derivative cluster amplitudes for different modes of perturbation. Calculation of second order properties also becomes cost effective as these can be obtained only with the knowledge of cluster amplitudes, eigen vectors and their first derivatives with respect to field and a additional set of perturbation independent vectors, i.e. the Λ -vectors.

3.4 Implementational details

We have used the ground state Hartree Fock as the vacuum for our calculation. In our study we have used singles and doubles approximation the Fock space cluster amplitudes (T) as well as Λ amplitudes for all these sectors. To solve the $(0, 1)$, $(1, 0)$ and $(1, 1)$ sector amplitudes, we first store the $(He^{T^{(0,0)}})_c$, which is called \bar{H} . The closed part of \bar{H} , i.e. \bar{H}_{cl} is the ground state energy. The open parts of \bar{H} can further be classified into one body, two body, three body parts and so on. Under the singles and doubles (SD) approximation, only up to three body parts of \bar{H} contribute to the $T^{(0,1)}$, $T^{(1,0)}$ and $T^{(1,1)}$ as well as to the $\Lambda^{(0,1)}$, $\Lambda^{(1,0)}$ and $\Lambda^{(1,1)}$ equations. The Jacobi iterative procedure has been used for the calculation of Λ amplitudes as well as all Fock space cluster amplitudes. To test the analytic non-relaxed CVA-FSMRCC code, we have carried out finite field non-relaxed FSMRCC calculation. To perform this, we have introduced finite field perturbation after the SCF procedure. Thus, the orbitals used for different field values are same. Dipole moments and polarizabilities were calculated as the first and second energy derivatives in the finite field non-relaxed calculation using three and five points respectively in steps of ± 0.001 au. Further, we have compared the results of our analytic non-relaxed code with relaxed finite field FSMRCC results. For the latter, field perturbation was introduced at the SCF level itself. Dipole moment was calculated using three point formula. However, polarizability was obtained as finite differences of the dipole moments. We have also compared our results with EOMCC results. EOMCC dipole moment was calculated in non-relaxed way while, polarizability was obtained as finite differences of dipole moments in relaxed way. EOMCC calculations were performed using Q-chem [60] system of program.

3.5 Results and discussion

In this section, some preliminary applications of non-relaxed CVA-FSMRCC method is presented for properties of both singlet and triplet low-lying excited states of water, ozone, HF and CH^+ molecule. CVA-FSMRCC results are compared with the non-relaxed finite-field FSMRCC results to perform the test of the code using CH^+ as a test molecule which is discussed in section 3.5.1. The basis set convergence study using CH^+ molecule in the basis of progressively higher accuracy is presented in section 3.5.2. Finally, the comparison of CVA-FSMRCC theory with the orbital relaxed finite-field FSMRCC (FF-FSMRCC) and EOM-CC is carried out for water, HF and ozone molecule. These reflect the importance of the effects of orbital relaxation for properties of excited states and the nonequivalence of CVA-FSMRCC and EOM-CC for the higher valence (more than one). For water molecule, the effect of the geometric relaxation is also studied through the comparison of the results of excited states using the ground state geometry as well as those of the excited state geometries. These results are presented in section 3.5.3.

3.5.1 Comparison of CVA-FSMRCC results with non-relaxed finite field

Dipole moments and polarizabilities of excited states of the carbon mono-hydride cation are presented in Table 3.1 using analytic Lagrangian based FSMRCC and finite field non-relaxed FSMRCC in two different basis sets, cc-pVDZ and Sadlej-pVTZ. Analytic dipole moments and polarizabilities along the molecular axis at the equilibrium geometry [64] is reported for triplet and singlet excited states formed by $\sigma^+ \rightarrow \pi$ transition. RHF of CH^+ is chosen as vacuum. HOMO (σ^+) is chosen as an active hole and two-fold degenerate LUMO (π) orbitals is chosen as active particles. Analytic FSMRCC

Table 3.1: Comparison of dipole moment and polarizabilities of carbon monohydride cation in lowest excited states with non-relaxed finite-field. Z-axis is molecular axis.

Basis	method	Dipole (singlet)	Dipole (triplet)	Polarizability (singlet)	Polarizability (triplet)
cc-pVDZ	CVA-FSMRCC	0.590204	0.418398	8.755014	8.336922
	FF-FSMRCC (non-relaxed)	0.590205	0.418392	8.755009	8.336915
Sadlej-pVTZ	CVA-FSMRCC	0.582694	0.423654	9.575564	9.221496
	FF-FSMRCC (non-relaxed)	0.582688	0.423647	9.575569	9.221490

All results are in atomic units.

dipole moments and polarizabilities for both singlet and triplet excited states are in good agreement with the FF-FSMRCC non-relaxed values. This agreement of results in both approaches serves as a test of the analytic FSMRCC code.

3.5.2 Study of basis set convergence

To study the basis set convergence, Double Zeta (Dunning) and Triple Zeta (Dunning) basis are chosen and then gradually added polarization functions (Pople polarization functions) up to $2p+1d$ for hydrogen and $2d+1f$ for carbon atom to reach the expansion limit. Results are presented in Table 3.2. It is observed that both singlet and triplet state dipole moments increase from DZ to TZ basis, DZP to TZP basis and so on, but the trend is just the opposite for polarizabilities. It is also observed that singlet dipole moments decrease with the addition of polarization functions, where as triplet dipole

Table 3.2: Dipole moment and polarizabilities of carbon monohydride cation in lowest excited states. Basis set convergence study. Z-axis is molecular axis.

Basis	Dipole (singlet)	Dipole (triplet)	Polarizability (singlet)	Polarizability (triplet)
DZ	0.669	0.384	7.54	7.90
DZ+P(H-1p/C-1d)	0.625	0.430	8.02	8.01
DZ+2P(H-2p/C-2d)	0.601	0.438	8.78	8.69
DZ+3P(H-2p,1d/C-2d,1f)	0.602	0.440	8.79	8.73
TZ	0.681	0.405	6.83	7.76
TZ+P(H-1p/C-1d)	0.656	0.432	7.18	7.79
TZ+2P(H-2p/C-2d)	0.607	0.449	8.52	8.64
TZ+3P(H-2p,1d/C-2d,1f)	0.606	0.450	8.51	8.65

All results are in atomic units.

mements increase with the addition of polarization functions. However, polarizabilities of both singlet and triplet states increase with the addition of polarization funcions. The dipole moments and polarizabilities of both the states are virtually converged after the addition of a second polarization function.

3.5.3 The study of relaxation effects and comparison with EOM-CC

As mentioned earlier, in this section dipole moment and polarizability of water and

ozone are presented calculated using CVA-FSMRCC, relaxed FF-FSMRCC and EOM-CC method. EOM-CC dipole moments reported here are non-relaxed while polarizabilities are orbital relaxed. For water molecule, the results for vertical excitation and adiabatic excitation are presented separately.

water molecule

Low-lying excited states of water exhibit strong MR character. Hence, this system is chosen for testing the efficiency of CVA-FSMRCCSD method. The results for the components of dipole moments and diagonal polarizabilities along the C_{2v} axis is presented using ground state geometry, results presented in Table 3.3, and using respective excited state geometries, results are in Table 3.4. For both these studies, Sadlej-pVTZ basis is used. For ground state geometry, dipole moments and polarizabilities of 1^1B_1 , $1^3B_1, 1^1B_2$, 1^3B_2 , 1^1A_2 , 1^3A_2 , 2^1A_1 and 2^3A_1 states are reported. The RHF ground state electronic configuration of water is

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 3sa_1^0 3pb_2^0 \dots$$

The orbitals $1b_1^2$ and $3a_1^2$ are the highest and second highest occupied MOs which are close-lying in energy and considered as active holes. Similarly, the orbitals $3sa_1$ and $3pb_2$ are near-degenerate active particles. The excited states of water, namely, $2A_1$, $1B_1$, $1B_2$ and $1A_2$ are dominated by the excitations $3a_1 \rightarrow 3sa_1$, $1b_1 \rightarrow 3sa_1$, $3a_1 \rightarrow 3pb_2$ and $1b_1 \rightarrow 3pb_2$ respectively.

The negative sign in the dipole moment values (ground state SCF dipole moment is 0.789997 a.u.) for all these states indicates the change in the orientation of the dipole moment with respect to the ground state due to the electronic excitation. CVA-FSMRCC dipole moment values for all the singlet excited states, except 2^1A_1 , are lower than the corresponding FF-FSMRCC values. But for the triplet excited states,

Table 3.3: Dipole moments and polarizabilities of water in low-lying excited states in sadlej-pVTZ basis set. Z-axis is molecular axis.

State	μ_z		α_{zz}	
	(CVA-FSMRCC)	(FF-FSMRCC)	(CVA-FSMRCC)	(FF-FSMRCC)
2^1A_1	-0.591	-0.576	72.41	67.46
1^1B_1	-0.645	-0.654	60.45	63.14
1^1B_2	-0.745	-0.778	32.52	28.24
1^1A_2	-0.579	-0.583	33.65	35.28
2^3A_1	-0.814	-0.784	58.76	52.55
1^3B_1	-0.451	-0.440	47.48	49.07
1^3B_2	-0.663	-0.610	27.38	28.04
1^3A_2	-0.588	-0.539	30.53	29.23

Ground state geometry used.
All results are in atomic units.

CVA-FSMRCC values are higher than the corresponding FF-FSMRCC values. In general, differences between the corresponding CVA-FSMRCC and FF-FSMRCC values are small indicating negligible orbital relaxation effect on dipole moment of the excited states considered here for water molecule.

Turning the attention to the polarizability values, it is observed that there is no general trend. In some cases, CVA-FSMRCC values are higher than the corresponding FF-FSMRCC values, in some other cases, the situation is just the reverse, though, the differences are within 10-15 percent. It is expected, because, polarizability is the second order response of energy. Hence, the orbital relaxation effect is large.

Table 3.4: Excited state dipole moment and polarizability of water using excited state geometry. Z-axis is molecular axis.

Basis	State	Property	Analytic FSMRCCSD	FF-FSMRCCSD	EOMCC[38]
Sadlej-pVTZ	1^1B_1	μ_z	-0.550	-0.540	-0.529
		α_{zz}	44.83	45.32	43.46
	1^3B_1	μ_z	-0.392	-0.401	-0.408
		α_{zz}	45.22	44.05	43.85

All results are in atomic units.

Among eight excited states of water molecule mentioned in Table 3.3, properties of only two excited states, 1^1B_1 and 1^3B_1 , are calculated using the respective optimized geometry [58] in sadlej-pVTZ basis set. This is been done to show the effect of geometrical relaxation. These results are presented in Table 3.4. Here, corresponding EOM-CC results are also presented.

It is observed that, the singlet state dipole moment value using FSMRCC methods (CVA-FSMRCC and finite-field FSMRCC) are higher compared to the EOM-CC value, but for the triplet state FSMRCC values are lower than the corresponding EOM-CC value. The values of polarizabilities of the singlet and the triplet states using FSMRCC are larger compared to the EOM-CC values. This discrepancy is due to the fact that though, for one valence problem, FSMRCC and EOM-CC are equivalent, the same is not true for higher valence problem. Differences between non-relaxed analytic FSMRCC values and relaxed finite-field FSMRCC values are due to the orbital relaxation effect. However, due to the cluster operators involving singly excited amplitudes, the orbital relaxation effects are not pronounced at least for those low-lying states. For the singlet

state, the absolute value of dipole moment decreases due to the relaxation effect while polarizability increases due to the same effect. For the triplet state, the effect of relaxation is just the opposite. Analytic FSMRCC dipole moment value for the triplet state is less than the corresponding finite-field value, where the polarizability value for non-relaxed FSMRCC is higher than relaxed FSMRCC value. Comparing CVA-FSMRCC dipole moment and polarizabilities of the singlet and the triplet excited B_1 states presented in Table 3.3 and Table 3.4, it is observed that the effect of geometric relaxation reduces dipole moments and polarizabilities of both the singlet and the triplet excited states.

Excited state properties of hydrogen mono-fluoride

Another important application of CVA-FSMRCC methods is done for hydrogen mono-fluoride molecule. It is an important compound for inorganic chemist. Ground state of HF molecule has two-fold degenerate π orbitals as HOMO and one σ^u as LUMO. Closed ground state Hartree-Fock configuration is taken as Fock space vacuum for this calculation. Two-fold π HOMO orbitals are taken as active hole and LUMO as active particle. The excited state considered here is formed due to the electronic transition from π to σ . HF bond length is taken as 1.7391 a.u. Sadlej-pVTZ basis is used for this calculation. Calculated results are presented in Table 3.5.

The CVA-FSMRCC dipole moment for both the singlet and the triplet are very close to the corresponding EOM-CC values where the orbital relaxed FF-FSMRCC values are marginally lower than the corresponding analytic values which may due to the orbital relaxation effect. The same trend is observed for the polarizabilities. Both dipole moment and polarizability of the singlet state are higher than the corresponding values of the triplet state.

Table 3.5: Dipole moment and polarizabilities of hydrogen monofluoride in lowest excited states. Z-axis is molecular axis.

Basis	State	Property	CVA-FSMRCCSD	FF-FSMRCCSD	EOMCC
Sadlej	$(\pi \rightarrow \sigma^u)$ triplet	μ_z	1.267	1.183	1.226
		α_{zz}	55.38	50.47	54.65
	$(\pi \rightarrow \sigma^u)$ singlet	μ_z	1.113	1.084	1.111
		α_{zz}	45.89	42.29	46.97

All results are in atomic units.

Excited state properties of ozone

Ozone represents an example with strong multi-configurational nature for which electric properties are rather poorly described at the SCF level. A lot of theoretical and experimental studies has been done so far for energies and geometries for the ground and excited states of ozone. However, there is no report of the excited state properties of ozone, in particular, polarizabilities. Excited state polarizabilities of ozone calculated using CVA-FSMRCC and EOM-CC methods are presented in Table 3.6.

The ground state geometry is used for this calculation. The ground state symmetry of ozone is A_1 and the electronic configuration of ozone for this state is

$$[core]3a_1^2, 2b_2^2, 4a_1^2, 5a_1^2, 3b_2^2, b_1^2, 4b_2^2, 6a_1^2, 1a_2^2, 2b_1^0, 7a_1^0 \dots$$

Excited states considered here are singlet and triplet states of B_2 , B_1 and A_2 , which are dominated by the electronic transition of $1a_2 \rightarrow 2b_1$ and $6a_1 \rightarrow 2b_1$ and $4b_2 \rightarrow 2b_1$.

Table 3.6: Excited state polarizability of ozone using ground state geometry in DZP basis. Z-axis is molecular axis.

State	Property	Analytic FSMRCCSD	EOMCC[38]
1B_2	α_{zz}	7.84	7.71
3B_2	α_{zz}	7.96	7.93
1A_2	α_{zz}	8.32	8.37
3A_2	α_{zz}	8.17	8.25
1B_1	α_{zz}	8.47	8.79
3B_1	α_{zz}	7.96	7.16

All results are in atomic units.

Thus, to represent these states adequately in FSMRCC, $6a_1$, $4b_2$ and $1a_2$ orbitals are used as active holes and $2b_1$ orbital as active particle. As observed from Table 3.6, CVA-FSMRCC polarizabilities of all the states are in very good agreement with the EOM-CC values.

Table 3.7: Geometry of two specific excited states of ozone

State	Bond length	Bond angle
1^1B_2	2.565	108.4
1^3B_2	2.571	108.3

All results are in atomic units.

The dipole moments and polarizabilities for the singlet and the triplet B_2 states are

also reported at the corresponding excited state geometry. The geometries of the singlet and the triplet state of B_2 are described in Table 3.7. Again, these results are compared with the EOM-CC values. Table 3.8 reports the values of dipole moments and polarizabilities. The singlet B_2 dipole moment value is in good agreement with EOM-CC, while for the triplet state, the CVA-FSMRCC value is slightly lower compared to the EOM-CC value. However, it is seen that the polarizabilities are in good agreement with the EOM-CC polarizability values. It is also seen that polarizabilities are enhanced at the excited state geometries for CVA-FSMRCC as well as EOM-CC compared to the respective polarizabilities at the ground state geometry. This emphasizes the effect of geometry for the polarizabilities for this molecule.

Table 3.8: Excited state dipole moment and polarizability of ozone using excited state geometry in DZP+sp diffuse basis. Z-axis is molecular axis.

State	Property	Analytic FSMRCCSD	EOMCC[38]
1B_2	μ_z	0.185	0.122
	α_{zz}	13.99	13.73
3B_2	μ_z	0.144	0.160
	α_{zz}	13.11	12.43

All results are in atomic units.

3.6 Conclusion

In this chapter, analytic dipole moments and polarizabilities of few low-lying excited states of water, ozone, HF and carbon mono-hydride cation are presented using

fully size-consistent CVA-FSMRCC method. A very good agreement of the dipole moment and polarizability values calculated using Lagrangian based FSMRCC method and non-relaxed FF-FSMRCC method test the correctness of the analytic code. The basis set convergence of both the dipole moment and polarizability for the CVA-FSMRCC method is also shown. Using water and HF as example, the effect of orbital relaxation and geometric relaxation are shown. The comparison with EOM-CC shows marginal differences in the values. For ozone, comparison is made mainly with the EOM-CC results and there are general agreements. Differences with EOM-CC, where ever there, arise due to the different effects of $\exp(T_1)$ in EOM-CC and the full singles and doubles space compared to the effects incorporated in building of Fock-space effective Hamiltonian over a small sub-space.

It may, however, be mentioned that while the present developement does not include the change of atomic orbitals with respect to perturbation, such effects will be required to be incorporated for calculation of gradients and Hessians, etc.

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Chapter 4

First hyper-polarizability of open shell molecules and radicals

In this chapter, the implementation of CVA-FSMRCC method for the calculation of hyper polarizability of few doublet radicals, such as OH, OF, NO and NO₂, at the ground state is presented along with the theoretical discussion. The near degeneracy in ground state of these molecules demand multi-reference description of the wave function. Orbital-relaxed finite field FSMRCC values have been reported for comparison. In some cases, CVA-FSMRCC results have been compared with ROHF results.

4.1 Introduction

In chapter 2, implementation of the CVA-FSMRCC [1–7] is discussed for the calculation of dipole moment and polarizability of hydroxyl radical, oxygen mono-fluoride, nitric oxide and nitrogen dioxide, which are considered as one valence problem in FSMRCC [8–17]. In this chapter, first hyper-polarizability of such systems is described. First hyper-polarizability may be calculated as the third order energy derivative. It is mentioned in the earlier chapters that linear response approach in FSMRCC using constrained variation technique [18] follows $(2n+1)$ rule for the cluster amplitudes (T) and $(2n+2)$ rule for the Lagrange multipliers (Λ). Hence, for the calculation of third order response properties, both first derivative of T and Λ are required. In earlier implementations, computational developments for the evaluation of cluster amplitudes (T), Lagrange multipliers (Λ) and the first derivatives of T amplitudes were done. For the present implementation, computational development for the calculation of first derivatives of Λ is done along with the advancement of computational techniques for the calculation of hyper polarizability using the required parameters. The first derivatives of Λ amplitudes are evaluated taking the first derivatives of the first order Lagrangian with respect to the cluster amplitudes. Hyper-polarizability is, ofcourse, a frequency dependent property. However, in this study, only the static hyper polarizabilities are reported. Hydroxyl anion, oxygen mono-fluoride, nitric oxide and nitrogen dioxide are taken as test molecules. In section 4.2, CVA-FSMRCC theory for hyper polarizability of one valence problem is discussed. In section 4.3, computational details is presented followed by results and conclusion.

4.2 Theoretical back ground

The constraint variational approach in FSMRCC frame-work for evaluation of response properties has been discussed in details in various articles [2, 4–7]. In this chapter, a brief description is given only for third order response properties.

The universal wave operator for one valence problem is given as

$$\Omega = \{e^{T^{(0,0)}} e^{T^{(0,1)}}\} \quad (4.1)$$

for one hole system and

$$\Omega = \{e^{T^{(0,0)}} e^{T^{(1,0)}}\} \quad (4.2)$$

for one particle system.

Under singles and doubles (SD) approximation, the cluster amplitudes (T) of every sector will contain only one-body and two-body parts. Following Mukherjee [9, 17], Sinha *et. al.* [10] and Pal *et. al.* [16] the above valence universal cluster operator satisfies Bloch equation.

$$H\Omega P^{k,l} = \Omega \tilde{H}_{eff}^{k,l} P^{k,l}; \forall k, l = 0, 1 \quad (4.3)$$

where, $\tilde{H}_{eff}^{(1,1)}$ includes contributions from all of the lower sector effective Hamiltonians in addition to the highest sector part. The diagonalization of the effective Hamiltonian yields the roots, which are the energies of the corresponding exact states. Due to normal ordering, sub-system embedding condition (SEC) holds and hence lower order cluster amplitudes decoupled from higher order cluster amplitudes. Thus evaluation of cluster amplitudes should start from the lowest sector i.e. (0,0) sector.

Calculation of response properties using CVA-FSMRCCSD includes the formation of Lagrangian which brings a new parameter Λ , the Lagrange multiplier. CVA-FSMRCC formalism was done by Shamasundar *et al.* [2]. The general expressions for the first,

second and third order derivatives for one valence problem have been presented in appendix of reference [2]. The Lagrangian for one valence problem for first and second order response properties have been presented by Manohar and Pal [5] and Bag *et al.* [6]. Thus, in this chapter, only the Lagrangian for third order response properties of one valence problems are presented.

The expression for hyper-polarizability of (0,1) sector is given bellow

$$\begin{aligned}
\mathfrak{S}_{opt}^{(3)} = & \left(\tilde{C}^{(0,1)(0)} (H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(3)} C^{(0,1)(0)} \right)_{m,m} \\
& + P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(3)}] P^{(0,1)} \\
& + 3P^{(0,1)} \Lambda^{(0,1)(1)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(2)}] P^{(0,1)} \\
& + P^{(0,0)} \Lambda^{(0,0)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)}] P^{(0,0)} \\
& + 3P^{(0,0)} \Lambda^{(0,0)(1)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)}] P^{(0,0)} \\
& + 6 \sum_{i,j} \tilde{C}_{mi}^{(0,1)(1)} (H_{eff}^{(0,1)})_{i,j}^{(1)} C_{jm}^{(0,1)(1)} - 6E_m^{(1)} \sum_i \tilde{C}_{mi}^{(0,1)(1)} C_{im}^{(0,1)(1)} \\
& + 3[(H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(2)}]_{mm} \left(\sum_i \tilde{C}_{mi}^{(0,1)(1)} C_{im}^{(0,1)(0)} + \sum_i \tilde{C}_{mi}^{(0,1)(0)} C_{im}^{(0,1)(1)} \right)
\end{aligned} \tag{4.4}$$

For (1,0) sector, expression for hyper-polarizability is exactly same as (0,1) sector only in place of (0,1) it would be (1,0).

4.3 Implementational details

For one valence problems nearest ionized or electron attached states should be chosen for SCF calculation which is the reference vacuum for FSMRCC. In general, results are invariant with respect to the choice of vacuum. However, it is necessary to mentioned that the vacuum should be chosen in a way such that required Fock space would be the lowest

sector among all other possibilities and would be of same symmetry as target molecule. As it is mentioned earlier, using SEC, cluster amplitudes are evaluated starting from (0,0) sector to the highest sector but Λ amplitudes are calculated exactly in the reverse order. To solve (0, 1) and (1, 0) sector amplitudes, first $(He^{T^{(0,0)}})_c$ is stored, which is called \bar{H} . The closed part of \bar{H} , i.e. \bar{H}_{cl} is the ground state energy. Open parts of \bar{H} can further be classified into one body, two body, three body parts and so on. Under the singles and doubles (SD) approximation, only up to three body parts of \bar{H} contribute to $T^{(0,1)}$ and $T^{(1,0)}$ as well as to $\Lambda^{(0,1)}$ and $\Lambda^{(1,0)}$ equations. Following (2n+1) rule for cluster amplitudes and (2n+2) rule for Λ amplitudes, derivatives of both these parameters are required for third order response properties and hence they are evaluated for calculation of hyper-polarizability. The Jacobi iterative procedure is used for the calculation of Λ and $\Lambda^{(1)}$ amplitudes as well as all Fock space cluster amplitudes. Ground state geometries of target molecules are used for SCF calculation. Results of analytic non-relaxed CVA-FSMRCC values are compared with non-relaxed finite-field results as well as relaxed finite-field FSMRCC results. For the latter, field perturbation is introduced at the SCF level itself. Relaxed finite field hyper-polarizabilities are calculated as finite differences of polarizabilities using three points in steps of ± 0.001 au finite field.

4.4 Results and discussion

In this section, applications of non-relaxed CVA-FSMRCC method is presented for the calculation of static hyper-polarizability of few doublet radicals; OH, OF, NO and NO₂. All of these molecules have unpaired electron in ground state electronic configuration and hence ionized or electron attached states of these molecules have closed shell electronic configuration. With respect to the closed shell configuration mentioned above,

respective molecule may be considered as one valence system. For testing the correctness of analytic code, CVA-FSMRCC hyper-polarizability of OH and NO molecules are compared with non-relaxed finite-field FSMRCC results. As stated in chapter 3, for non-relaxed finite-field calculation, field perturbation is introduced after SCF calculation. Comparison fo CVA-FSMRCC with relaxed finite-field FSMRCC for OH, OF, NO and NO₂ molecules is also studied.

4.4.1 testing of analytic code

OH radical may be treated as one hole problem in Fock space with respect to the RHF determinant of OH⁻ as vacuum. Thus, this radical is taken as test example for testing the correctness of the (0,1) sector code for the calculation of first static hyper-polarizability. Similarly, nitric oxide (NO), which may be treated as one particle problem in FSMRCC with respect to the RHF determinant of NO⁺, is used for the same for (1,0) sector code. Results are given in Table 4.1.

Table 4.1: First hyper-polarizability of OH radical and NO molecule. Comparison with non-relaxed finite field FSMRCC results. Z-axis is molecular axis.

Molecule	Basis	Property	CVA-FSMRCC	FF-FSMRCC
NO	aug-cc-pVDZ	β_{zzz}	-11.99	-12.01
	Sadlej-pVTZ	β_{zzz}	-13.82	-13.80
OH	aug-cc-pVDZ	β_{zzz}	-17.55	-17.51
	Sadlej-pVTZ	β_{zzz}	-12.86	-12.87

All results are in atomic units.

Two-fold degenerate HOMO of OH⁻ radical is chosen as active holes. O-H bond

length used for this calculation is 1.85104 a.u. Two-fold degenerate (π) LUMO orbitals of NO^+ are chosen as active particles. Addition of one electron in one of the active orbitals result in the formation of the corresponding molecule. Hyper-polarizability for the $^2\Pi$ state of NO molecule is reported here. N-O bond distance, used for this calculation, is 2.155 a.u. Two different basis sets; aug-cc-pVDZ and Sadlej-pVTZ are used for both these test examples. For all cases, CVA-FSMRCC results match up to the second decimal point with the non-relaxed finite-field FSMRCC results. As, for the calculation of the non-relaxed FF-FSMRCC, third order finite derivative of energy is used, following five point formula in the stapes of ± 0.001 a.u. field, finite-field results are only correct up to the second decimal point.

4.4.2 study of relaxation effect

In this section, CVA-FSMRCC hyper-polarizability results for OF, OH, NO and NO_2 molecules are compared with relaxed finite-field FSMRCC results. For the calculation of relaxed FF-FSMRCC, as usual, field perturbation is introduced in the SCF level, hence, for every field value atomic orbitals are different, perturbed by the applied field. As mentioned in the implementation section, for relaxed FF-FSMRCC calculation, finite differences of CVA-FSMRCC polarizabilities are used.

Oxygen mono-fluoride molecule

Oxygen mono-fluoride molecule can be viewed as ionized state of oxygen mono-fluoride anion resulting from removal of an electron from the HOMO which has π character. Thus, for FSMRCC calculations, RHF of oxygen mono-fluoride anion was chosen as vacuum. With respect to this vacuum, ground state of OF molecule may be considered as one hole problem. Two-fold degenerate HOMO was taken as active orbitals. For SCF

calculation, ground state geometry of OF was used ($R_{eq} = 2.5953a_0$) [19]. The aug-cc-pVDZ and sadlej-pVTZ basis sets have been used for calculation. Calculated results are presented in Table 4.2.

Table 4.2: Comparison of CVA-FSMRCC hyper-polarizability values of OF molecule with orbital relaxed finite field values. Z-axis is molecular axis.

Basis	Property	CVA-FSMRCCSD	FF-FSMRCC
aug-cc-pVDZ	β_{zzz}	-18.75	-18.53
	$\beta_{yyy} = \beta_{xxx}$	0.02	0.00
sadlej-pVTZ	β_{zzz}	-41.99	-43.70
	$\beta_{yyy} = \beta_{xxx}$	0.05	0.01

All results are in atomic units.

Here, both CVA-FSMRCCSD and FF-FSMRCCSD values were very close which indicate that orbital relaxation effect is less for this molecule. It was also found that hyper-polarizability component along molecular axis is larger than two other components reported here. It is obvious that as OF is linear $\beta_{xxx} = \beta_{yyy}$.

OH radical

For the calculation of hyper-polarizability of OH radical, same geometry and basis sets are used as mentioned earlier. Calculated hyper-polarizabilities of OH molecule are presented in Table 4.3.

As expected, hyper-polarizability values of OH molecule along molecular axis were very large compare to that of perpendicular to molecular axis. It is obvious that as OH molecule is linear, $\beta_{xxx} = \beta_{yyy}$. For OH molecule, CVA-FSMRCCSD values widely

Table 4.3: Comparison of CVA-FSMRCC hyper-polarizability values of OH molecule with orbital relaxed finite field values. Z-axis is molecular axis.

Basis	Property	CVA-FSMRCCSD	FF-FSMRCC
aug-cc-pVDZ	β_{zzz}	-17.55	-22.50
	$\beta_{yyy} = \beta_{xxx}$	0.06	0.01
sadlej-pVTZ	β_{zzz}	-12.86	-17.14
	$\beta_{yyy} = \beta_{xxx}$	0.01	0.00

All results are in atomic units.

differs from FF-FSMRCCSD values which shows significant contribution of orbital relaxation effect for finite field calculation.

Nitric oxide molecule

For the calculation of hyper-polarizability of NO molecule, same geometry and basis sets are used mentioned earlier. Calculated results are presented in Table 4.4. For linear NO molecule, $\beta_{xxx} = \beta_{yyy}$. Again, hyper-polarizability components perpendicular to molecular axis are found to be very small compare to that of the principal axis.

Here, differences of hyper-polarizability values between two methods are significant hence orbital relaxation is large for this molecule. It was found that CVA-FSMRCCSD values were nearly same for two different basis sets which is not true for FF-FMRCCSD method.

Table 4.4: Components of hyper-polarizability of NO molecule. Comparison with orbital relaxed finite field FSMRCC results. Z-axis is molecular axis.

Basis	Property	CVA-FSMRCC	FF-FSMRCC
aug-cc-pVDZ	β_{zzz}	-11.99	-16.41
	$\beta_{xxx} = \beta_{yyy}$	0.01	0.00
Sadlej-pVTZ	β_{zzz}	-13.82	-21.30
	$\beta_{xxx} = \beta_{yyy}$	0.03	0.02

All results are in atomic units.

Nitrogen dioxide molecule

For NO₂ molecule, NO₂⁺ is used as reference vacuum. Ground state geometry [20] is used for RHF calculation. LUMO of NO₂⁺ is a σ orbital but there is another σ orbital in virtual space which is very close in energy to LUMO and hence these two orbitals are chosen as active particles. cc-pVDZ basis and DZP basis with sp diffuse functions are used for this calculation. Calculated results are presented in Table 4.5. As NO₂ is a non-linear molecule three principal components of hyper-polarizability are presented. Hyper-polarizability component along principal axis is higher than two other components presented here. The most important fact, which is found from this calculation, is that hyper-polarizability of this molecule is positive which means that direction of hyper-polarizability is opposite to its dipole moment.

Hyper polarizability values were very small for this molecule for cc-pVDZ basis and also the relaxation effect. For DZP basis with sp diffuse function hyper-polarizability values increase significantly which due to the inclusion of diffusion function. Effect of

Table 4.5: Components of hyper-polarizability of nitrogen dioxide molecule. Comparison with orbital relaxed finite field FSMRCC results. Z-axis is molecular axis.

Basis	Property	CVA-FSMRCC	FF-FSMRCC
cc-pVDZ	β_{zzz}	4.34	6.33
	β_{xxx}	0.27	0.05
	β_{yyy}	0.22	0.04
DZP+sp	β_{zzz}	8.38	8.69
	β_{xxx}	1.06	0.25
	β_{yyy}	0.92	0.17

All results are in atomic units.

orbital relaxation is prominent for this basis.

4.5 Conclusion

In this chapter, analytic hyper-polarizability of OH, OF, NO and NO₂ molecules is computed using CVA-FSMRCC method. CVA-FSMRCC values are compared with orbital non-relaxed finite-field FSMRCC values for testing the analytic code and with orbital relaxed finite-field FSMRCC results to show the orbital relaxation effect. It is found that molecules with larger values of hyper-polarizabilities show significant orbital relaxation effect. Except OF molecule, for all three other molecules relaxation effect is large. It is also found that for all test molecules direction of hyper-polarizability is same as that of dipole moment except NO₂ molecule where direction is just opposite.

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Chapter 5

First hyper-polarizability of closed shell molecules at the excited states

The first and the second order response properties of the singlet and the triplet excited states of closed shell molecules using CVA-FSMRCCSD method are presented in chapter 3. In this chapter, third order response properties, hyper-polarizability, of the singlet and the triplet excited states of closed shell molecules are presented using CVA-FSMRCCSD method. Theoretical developments for hyper-polarizability calculation of the low-lying excited states of closed shell molecules are discussed. Diagonal components of hyper-polarizabilities of low-lying excited states of ozone and water are presented. Basis set convergence is studied for CH^+ molecule.

5.1 Introduction

Implementation of CVA-FSMRCC [1–7] method for the calculation of the first static hyper-polarizability of the low-lying electronic excited states of closed shell molecules are presented in this chapter. The low-lying electronic excited states of closed shell molecules are dominated by single hole particle excited determinants with respect to the restricted Hartree-Fock of the ground state. These constitute the (1,1) sector of Fock-space [8–17]. In chapter 3, it is described that (1,1) sector property calculation involves the calculation of lower (0,1), (1,0) and (0,0) sectors. Computational developments and implementation of CVA-FSMRCCSD method for the hyper-polarizability calculation of (0,1) and (1,0) sectors have been described in chapter 4. In chapter 3, implementation of CVA-FSMRCCSD method for calculation of dipole moment and polarizability of the singlet and the triplet excited states of closed shell molecules have been presented. This involves evaluation of $T^{(1,1)}$, $\Lambda^{(1,1)}$ and $T^{(1,1)}$ derivatives. But, for hyper-polarizability calculation, $\Lambda^{(1,1)}$ derivatives are also required following $(2n + 2)$ rule for Λ . For (1,1) sector, there is a partial decoupling of the Fock space sectors due to the SEC. (1,1) sector cluster amplitudes ($T^{(1,1)}$) as well as Lagrange multipliers ($\Lambda^{(1,1)}$) are of two different types, direct and exchange types (see the diagrams of reference [5]). For the calculation of the triplet excited states properties, only direct types are required, but for the singlet state properties both direct and exchange types are required. For the present study, computational developments are done for the calculation of hyper-polarizability of both the singlet and the triplet excited states.

CVA-FSMRCC ansatz for the excited states have been mostly covered in chapter 3. In this chapter, the expressions for the third order response properties for the electronic excited states (singlet and triplet) described by (1,1) FS sector are given in section 5.2.

This is followed by implementational details, discussion of results and conclusion. In the results and discussion section, non-relaxed finite-field FSMRCC results are presented as a test of the analytic code. Comparison of CVA-FSMRCC with relaxed finite-field FSMRCC and EOM-CC [18–34] results are also presented.

5.2 Theoretical back ground

The constrained variational approach in FSMRCC frame-work based on Lagrange formulation has been discussed in detail in various articles [2, 4–7]. In this chapter, CVA-FSMRCCSD method is described for hyper-polarizability calculation of the singlet and the triplet excited states of closed molecules.

The universal wave operator for (1,1) sector of Fock space is given as

$$\Omega = \{e^{T^{(0,0)}} e^{T^{(0,1)}} e^{T^{(1,0)}} e^{T^{(1,1)}}\} \quad (5.1)$$

Under the singles and doubles (SD) approximation, the cluster amplitude T of every sector will contain only one-body and two-body operators. Following Mukherjee [9, 17], Sinha *et. al.* [10] and Pal *et. al.* [16] the above valence universal cluster operator satisfies Bloch equation.

$$H\Omega P^{k,l} = \Omega \tilde{H}_{eff}^{k,l} P^{k,l}; \forall k, l = 0, 1 \quad (5.2)$$

where, $\tilde{H}_{eff}^{(1,1)}$ includes contributions from all of the lower sector effective Hamiltonians in addition to the highest sector part. The diagonalization of the effective Hamiltonian yields the roots, which are the energies of the corresponding exact states. Due to normal ordering, sub-system embedding condition (SEC) holds and hence lower order cluster amplitudes decoupled from higher order cluster amplitudes. Thus evaluation of cluster amplitudes should starts from the lowest sector i.e. (0,0) sector.

Calculation of response properties using CVA-FSMRCCSD includes the formation of Lagrangian which brings a new parameter Λ , the Lagrange multiplier. CVA-FSMRCC formalism was done by Shamasundar *et al.* [2]. The general expressions for the first, second and third order derivatives for both one valence and two valence problem were given in appendix of reference [2]. For excited states there are an additional decoupling between the singlet and the triplet exists due to spin integration. This decoupling was discussed by Manohar and Pal [4]. The Lagrangian for first and second order response properties for excited states have also been presented by Manohar and Pal [4] and Bag *et al.* [7]. Thus, in the present discussion, only the Lagrangian for third order response properties of two valence problem has been presented.

For the triplet excited states expression for hyper-polarizability is as follows

$$\begin{aligned}
\mathfrak{S}_{opt}^{(3)} = & \left(\tilde{C}^{(1,1)(0)} (H_{eff}^{(1,1)T})_{\Omega^{(1)}}^{(3)} C^{(1,1)(0)} \right)_{m,m} \\
& + P^{(1,1)} \Lambda^{(1,1)(0)D} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(1,1)T})_{\Omega^{(1)}}^{(3)}]^D P^{(1,1)} \\
& + 3P^{(1,1)} \Lambda^{(1,1)(1)D} [H^{(1)} \Omega_{\Omega^{(1)}}^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(1,1)T})_{\Omega^{(1)}}^{(2)}]^D P^{(1,1)} \\
& + P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(3)}] P^{(0,1)} \\
& + 3P^{(0,1)} \Lambda^{(0,1)(1)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(2)}] P^{(0,1)} \\
& + P^{(1,0)} \Lambda^{(1,0)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(1,0)})_{\Omega^{(1)}}^{(3)}] P^{(1,0)} \\
& + 3P^{(1,0)} \Lambda^{(1,0)(1)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(1,0)})_{\Omega^{(1)}}^{(2)}] P^{(1,0)} \\
& + P^{(0,0)} \Lambda^{(0,0)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)}] P^{(0,0)} \\
& + 3P^{(0,0)} \Lambda^{(0,0)(1)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)}] P^{(0,0)} \\
& + 6 \sum_{i,j} \tilde{C}_{mi}^{(1,1)(1)} (H_{eff}^{(1,1)T})_{i,j}^{(1)} C_{jm}^{(1,1)(1)} - 6E_m^{(1)} \sum_i \tilde{C}_{mi}^{(1,1)(1)} C_{im}^{(1,1)(1)} \\
& + 3[(H_{eff}^{(1,1)T})_{\Omega^{(1)}}^{(2)}]_{mm} \left(\sum_i \tilde{C}_{mi}^{(1,1)(1)} C_{im}^{(1,1)(0)} + \sum_i \tilde{C}_{mi}^{(1,1)(0)} C_{im}^{(1,1)(1)} \right)
\end{aligned} \tag{5.3}$$

for the singlet states expression is

$$\begin{aligned}
\mathfrak{S}_{opt}^{(3)} = & \left(\tilde{C}^{(1,1)(0)} (H_{eff}^{(1,1)S})_{\Omega^{(1)}}^{(3)} C^{(1,1)(0)} \right)_{m,m} \\
& + P^{(1,1)} \Lambda^{(1,1)(0)E} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(1,1)S})_{\Omega^{(1)}}^{(3)}]^E P^{(1,1)} \\
& + 3P^{(1,1)} \Lambda^{(1,1)(1)E} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(1,1)S})_{\Omega^{(1)}}^{(2)}]^E P^{(1,1)} \\
& + P^{(1,1)} \Lambda^{(1,1)(0)D} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(1,1)T})_{\Omega^{(1)}}^{(3)}]^D P^{(1,1)} \\
& + 3P^{(1,1)} \Lambda^{(1,1)(1)D} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(1,1)T})_{\Omega^{(1)}}^{(2)}]^D P^{(1,1)} \\
& + P^{(0,1)} \Lambda^{(0,1)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(3)}] P^{(0,1)} \\
& + 3P^{(0,1)} \Lambda^{(0,1)(1)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(0,1)})_{\Omega^{(1)}}^{(2)}] P^{(0,1)} \\
& + P^{(1,0)} \Lambda^{(1,0)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)} - (\Omega H_{eff}^{(1,0)})_{\Omega^{(1)}}^{(3)}] P^{(1,0)} \\
& + 3P^{(1,0)} \Lambda^{(1,0)(1)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)} - (\Omega H_{eff}^{(1,0)})_{\Omega^{(1)}}^{(2)}] P^{(1,0)} \\
& + P^{(0,0)} \Lambda^{(0,0)(0)} [H^{(1)} \Omega_{\Omega^{(1)}}^{(2)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(3)}] P^{(0,0)} \\
& + 3P^{(0,0)} \Lambda^{(0,0)(1)} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)}] P^{(0,0)} \\
& + 6 \sum_{i,j} \tilde{C}_{mi}^{(1,1)(1)} (H_{eff}^{(1,1)S})_{i,j}^{(1)} C_{jm}^{(1,1)(1)} - 6E_m^{(1)} \sum_i \tilde{C}_{mi}^{(1,1)(1)} C_{im}^{(1,1)(1)} \\
& + 3[(H_{eff}^{(1,1)S})_{\Omega^{(1)}}^{(2)}]_{mm} \left(\sum_i \tilde{C}_{mi}^{(1,1)(1)} C_{im}^{(1,1)(0)} + \sum_i \tilde{C}_{mi}^{(1,1)(0)} C_{im}^{(1,1)(1)} \right)
\end{aligned} \tag{5.4}$$

There are two types of cluster amplitudes as well as Lagrange multiplier (Λ) for (1,1) sector of FSMRCC as discussed in chapter 3 (see figure 3.1). In one type, there are no mixing between hole lines with particle lines and hence termed as direct type, denoted by ‘D’ in the above equation which is same as type ‘A’ in figure-1 of reference [4]. Other type includes mixing between hole lines and particle lines and termed as exchange type, denoted by ‘E’ and same as type ‘B’ of reference mentioned above. For the triplet excited states, only ‘D’ type cluster amplitudes and hence ‘D’ type Λ is required to be evaluated while for the singlet excited states both types of cluster amplitudes and Λ to be evaluated.

5.3 Implementational details

For (1,1) sector problems, ground state is closed shell electronic configuration and hence RHF of these state is generally chosen as reference vacuum. Due to subsystem embedding condition, cluster amplitudes were evaluated starting from (0,0) sector to the highest sector but Λ amplitudes were calculated exactly in the reverse order. To solve (1, 1) sector amplitudes, we first store $(He^{T^{(0,0)}})_c$, which is called \bar{H} . The closed part of \bar{H} , i.e. \bar{H}_{cl} is the ground state energy. The open parts of \bar{H} can further be classified into one body, two body, three body parts and so on. Under the singles and doubles (SD) approximation, only up to three body parts of \bar{H} contribute to $T^{(1,1)}$ as well as to $\Lambda^{(1,1)}$ equations. According to (n+1) rule for cluster amplitudes and (2n+2) rule for Λ amplitudes, derivatives of both these parameters were evaluated and used for calculation of third order response property. The Jacobi iterative procedure has been used for the calculation of Λ and $\Lambda^{(1)}$ amplitudes as well as all Fock space cluster amplitudes. To test the analytic non-relaxed CVA-FSMRCC code, finite field non-relaxed FSMRCC calculation was carried out. This was performed by introducing field perturbation after the SCF calculation. Thus, the orbitals used for different field values are same. Non-relaxed finite field hyper-polarizabilities were calculated as the third order energy derivatives using five points respectively in steps of ± 0.001 au. Further, analytic (non-relaxed CVA-FSMRCC) results are compared with relaxed finite field FSMRCC results. For relaxed finite field calculation, field perturbation was introduced at the SCF level itself. Relaxed finite field hyper-polarizabilities were calculated as finite differences of polarizabilities.

5.4 Results and discussion

In this section, static hyper polarizabilities of ozone (O_3), water (H_2O) and carbon mono-hydride cation (CH^+) are presented. For all these calculations, geometry and bases are same as mentioned in chapter 3. Here, again CH^+ molecule is taken for testing the correctness of the analytic code through the comparison with non-relaxed finite-field FSMRCC results and basis set convergence.

5.4.1 Validation of the code and basis set convergence study

Static hyper-polarizabilities of carbon mono-hydride cation for the singlet and the triplet states are given in Table 5.1 calculated using cc-pVDZ and Sadlej-pVTZ basis sets. Analytic values are compared with non-relaxed FF-FSMRCC values. For the calculation of non-relaxed FF-FSMRCC, same procedure as described in chapter 3, is followed. CVA-FSMRCC hyper-polarizabilities for both the singlet and the triplet excited states are in good agreement with non-relaxed FF-FSMRCC values. This agreement of results serves as a test of the analytic code. Here, results are reported up to the second decimal point due to the same reason described in chapter 4.

Table 5.1: Comparison of hyper polarizabilities of carbon monohydride cation in lowest excited states with non-relaxed finite field. Z-axis is molecular axis.

Basis	method	hyper Polarizability (singlet)	hyper Polarizability (triplet)
cc-pVDZ	CVA-FSMRCC	12.32	19.18
	FF-FSMRCC (non-relaxed)	12.38	19.16
Sadlej	CVA-FSMRCC	21.37	43.99
	FF-FSMRCC (non-relaxed)	21.32	43.91

All results are in atomic units.

For the study of the basis set convergence, same bases are used as mentioned in chapter 3. These results are presented in Table 5.2. It is observed that, for the singlet state, hyper-polarizability decreases from DZ to DZP, DZP to DZP+P and so on, but the opposite trend is observed for TZ to TZP, TZP to TZP+P and so on. Though, at the expansion limit, the values are very close. For the triplet state, hyper-polarizability decreases from DZ to DZP, TZ to TZP and so on. In this case also, at the expansion limit, values are very close.

Table 5.2: Hyper-polarizabilities of carbon monohydride cation in lowest excited states. Basis set convergence study. Z-axis is molecular axis.

Basis	Hyper-polarizability (singlet)	Hyper-polarizability (triplet)
DZ	45.65	76.77
DZ+P(H-1p/C-1d)	34.69	65.93
DZ+2P(H-2p/C-2d)	30.10	63.13
DZ+3P(H-2p,1d/C-2d,1f)	29.88	63.08
TZ	7.18	63.40
TZ+P(H-1p/C-1d)	8.91	57.71
TZ+2P(H-2p/C-2d)	24.09	54.40
TZ+3P(H-2p,1d/C-2d,1f)	24.41	53.51

All results are in atomic units.

5.4.2 Study of relaxation effect

To study the orbital relaxation effect, water molecule is taken as test example. Non-relaxed CVA-FSMRCC results are compared with the relaxed finite-field FSMRCC results. Hyper-polarizabilities of the singlet and the triplet excited B_1 states of water molecule are calculated using the respective excited state geometries [37]. Results are presented in Table 5.3. Sadlej-pVTZ basis is used for this calculation. Differences between non-relaxed analytic FSMRCC values and relaxed finite-field values are due to the

orbital relaxation effect. However, as the cluster operators involve singly excited amplitudes the orbital relaxation effects are not pronounced atleast for these lowlying states. Analytic value for the singlet excited state is less than the finite-field value, where the effect of orbital relaxation is opposite for the triplet state.

Table 5.3: Excited state hyper-polarizability of water using excited state geometry. Z-axis is molecular axis.

Basis	State	Property	CVA-FSMRCCSD	FF-FSMRCCSD
Sadlej-pVTZ	1^1B_1	β_{zzz}	44.14	47.20
	1^3B_1	β_{zzz}	39.31	35.23

All results are in atomic units.

5.4.3 Comparison with EOM-CC

It is stated earlier that, for one valence problem, FSMRCC and EOM-CC are equivalent but equivalence disappears for the higher valence problem.

Table 5.4: Excited state hyper-polarizability of ozone using ground state geometry in DZP basis. Z-axis is molecular axis.

State	Property	Analytic FSMRCCSD	EOMCC[18]
1B_2	β_{zzz}	8.07	6.53
3B_2	β_{zzz}	18.91	16.22
1A_2	β_{zzz}	6.56	5.55
3A_2	β_{zzz}	10.38	9.72
1B_1	β_{zzz}	9.26	7.05
3B_1	β_{zzz}	9.27	7.72

All results are in atomic units.

Still, the comparison between FSMRCC and EOM-CC make sense because both these methods produce very good results and are well established. Ozone molecule is used for this comparison. Calculation is done using ground state geometry in DZP basis. Details of this calculation are described in chapter 3. Results are presented in Table 5.4. Hyper-polarizabilities of all the states are in very good agreement with the EOM-CC values.

5.5 Conclusion

In this chapter, analytic FSMRCC hyper-polarizabilities of water, ozone and carbon mono-hydride cation are presented. Basis set convergence is studied and orbital relaxation effect is also studied. The marginal differences between CVA-FSMRCC and EOM-CC, where arises, may due to the different effects of $\exp(T_1)$ in EOM-CC and the full singles and doubles space compared to the effects incorporated in building of Fock-space effective Hamiltonian over a small sub-space. Hyper-polarizabilities are small for all the molecules tested here. For a molecule with larger value of hyper-polarizability the situation may differ.

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Summary and Scope of the thesis

The present work discusses about computational developments and implementation of FSMRCC response method based on Lagrange variation approach. Due to the multi-root nature, getting energy derivatives in FSMRCC frame-work was not trivial. Introduction of constrained variation approach (CVA) (Lagrange variation approach) in FSMRCC opens the door for calculation of response properties e.g. electric properties, magnetic properties, gradient, Hessians etc. Implementation of CVA was initiated by Manohar and Pal for calculation of dipole moments and polarizabilities of doublet radicals and the triplet excited states of closed shell molecules. In this thesis work, existing code was tested by comparing CVA-FSMRCC results with non-relaxed finite-field FSMRCC results. More applications were done using the previous code. New code is developed for calculation of dipole moment and polarizability of the singlet excited states of closed shell molecule. New code is also developed and implemented for calculation of hyper-polarizability of doublet radicals, the singlet and the triplet excited states of closed shell molecules.

So far, electrical properties are calculated using CVA-FSMRCC, but this approach can be extended to magnetic properties and properties related to geometric perturbation. This method may be used for excited state geometry optimization. It is also possible to calculate properties related to simultaneous perturbation of any two or all three of electric, magnetic and geometric perturbation.