# PROPERTIES OF MOLECULES IN GROUND AND LOW-LYING EXCITED STATES USING SOME STATIONARY COUPLED-CLUSTER METHODS

Thesis submitted to the
**University of Pune**
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**Doctor of Philosophy**
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By

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# CERTIFICATE

CERTIFIED THAT the work done in the thesis entitled,

Properties of molecules in ground and low-lying excited states using some stationary coupled-cluster methods

submitted by **Prashant Uday Manohar** was carried out by the candidate under my supervision in the Physical Chemsitry Division, National Chemical Laboratory, Pune 411008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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# DECLARATION

I hereby declare that the work incorporated in the thesis entiled

Properties of molecules in ground and low-lying excited states using some stationary coupled-cluster methods

submitted by me to **University of Pune** for the degree of Doctor of Philosophy is original and has not been submitted to this or other University or Institution for the award of Degree or Diploma. Such material, as has been obtained from other sources has been duly acknowledged.

Prashant Uday Manohar

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# Contents

# List of Tables

# List of Publications

1. “Extended coupled-cluster method for magnetizabilities of small molecules”

   - **P. U. Manohar**, N. Vaval, S. Pal;

   *Chem. Phys. Lett.* 387 (2004) 442-447.

2. “Electronic spectra and Ionization potentials of Halogen oxides using Fock-space coupled-cluster method”

   - N. Vaval, **P. Manohar**, S. Pal;

   *Collect. Czech. Chem. Commun.* 70 (2005) 851-863.

3. “Constrained variational response to Fock-space multi-reference coupled-cluster theory: Some pilot applications”

   - **P. U. Manohar**, N. Vaval, S. Pal;

   *J. Mol. Struct. THEOCHEM* 768 (2006) 91-96.

4. “Dipole moments and polarizabilities of some small radicals using constrained variational response to Fock-space multi-reference coupled-cluster theory”

   -**P. U. Manohar**, S. Pal;

   *Chem. Phys. Lett.*(communicated.)

5. “Optical properties of molecules in excited states using constrained variational Fock-space multi-reference coupled-cluster method”

   -**P. U. Manohar**, S. Pal;

   (in preparation.)

# Abstract

Coupled-cluster (CC) based methods [1] have emerged as the methods of choice for electronic structure calculations of highly correlated molecular systems due to the accuracy and size-extensivity. The molecules with non-degenerate ground state, for example, closed-shell molecules and some non-degenerate open-shell systems, can be studied accurately using single reference (SR) CC methods based on restricted (closed-shell) Hartree-Fock (RHF) or restricted open-shell Hartree-Fock (ROHF) configuration as starting wave-function, whereas, the degenerate and near-degenerate states of molecules can be well described by what are known as multi-reference (MR) CC [2] methods, incorporating the important non-dynamical electron correlation. The effective Hamiltonian versions of these have been well studied.

Standard CC methods have been developed using a non-variational approach. Analytical molecular properties as analytic energy derivatives have been studied thoroughly in the SRCC framework [3]. The introduction of Z-vector technique [4] and constrained-variational approach (CVA) [5] in SRCC framework has made it plausible to determine the higher order properties with the knowledge of lower order cluster amplitudes. Several stationary approaches in SRCC also have been there, which include expectation value coupled-cluster (XCC) [7], unitary coupled-cluster (UCC) [8] and extended coupled-cluster (ECC) [8, 9] methods. Of these methods, ECC is found to be a very efficient approach for evaluating molecular properties. The double-similarity transformed structure of the energy functional in ECC leads to a double-linked functional after an additional transformation on the right vectors. The double-linking of left vectors and connectedness of the right vectors to the Hamiltonian ensures connectedness and consequently the size-extensivity in the equations for the cluster amplitudes, which are obtained by making the energy functional stationary with respect to the left and the

right vectors respectively. As a consequence of the stationarity conditions, the left and right vectors obey Hellmann-Feynman theorem due to which there is a (2n+1) rule for evaluation of response properties.

Like other SRCC approaches, ECC has also been extensively studied for ground state electric properties [9] of closed-shell molecules. However, there have been much fewer implementations of these methods in obtaining magnetic properties of molecules. In the present thesis, we attempt to use ECC functional for calculating ground state magnetizabilities of closed-shell molecules using ECC linear response method.

The extension of linear response methods in calculation of magnetic properties is however, non-trivial. Evaluation of magnetic properties suffers from the serious drawback, namely, the so-called gauge-dependence. Several approaches have been used to eliminate this problem. Notable amongst them are use of gauge-including atomic orbitals (GIAO) [10], individual gauge for localized orbitals (IGLO) [11], polarization propagator approach [12], local origin method (LORG) [13], random phase approximation (RPA) [14], use of extended basis sets, etc. We attempt to do first implementation of ECC for evaluation of magnetizabilities of closed-shell molecules using Gaussian basis sets. This is a step towards formulation of the GIAO based ECC calculations of these properties. It is seen that with proper choice of gauge-origin, the magnetizabilities can be evaluated quite accurately.

The development of analytic energy derivatives in the effective Hamiltonian based MRCC framework has been a much recent topic of study. The complexity lied mainly in the multi-root nature of the MRCC methods. The problem of energy derivatives in the context of effective Hamiltonian versions of MRCC was first addressed by Pal [15] long back. However, it took a long time since then for a concrete formulation to appear. Development and implementation of non-variational linear response functional for the energy derivatives in Fock-space (FS) MRCC was done by Ajitha *et. al.* [16]. However, this was quite unsatisfactory as it involved the use of first derivatives of cluster amplitudes in the first energy derivatives. A more satisfactory formulation along the lines of SRCC analytic derivatives could be obtained only by using CVA technique.

Formulation of CVA technique in MRCC framework is non-trivial. Szalay [17] initiated this work in FSMRCC context and analysed the functional for gradient calculations. The method was, however, applicable only for complete model spaces (CMS). The CVA-FSMRCC technique for specific root of effective Hamiltonian was formulated by Pal and co-workers [18] and is applicable for general incomplete model spaces (IMS) also. The advantage of this method over the non-variational response method is elimination of perturbation dependent parameters in wave-functions in obtaining first order properties like dipole moment, magnetic moment, etc. Based on the Lagranges method of undetermined multipliers, in CVA, Lagrangian is constructed for specific root of effective Hamiltonian. In addition to cluster amplitudes, one has to solve only one additional set of linear equations for perturbation-independent amplitudes, i.e. the Lagrange multipliers. The cluster equations are obtained by making Lagrangian stationary with respect to the Lagrange multipliers, which are obtained by making Lagrangian stationary with respect to cluster amplitudes. The left and right eigen vectors of effective Hamiltonian are also obtained variationally. The cluster amplitudes are completely decoupled from 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. This is commonly referred to as subsystem embedding condition (SEC). The Lagrange multipliers are coupled with the cluster amplitudes; and due to stationarity condition, they are coupled within themselves in a reverse SEC manner. The cluster amplitudes and eigen vectors follow $(2n + 1)$ rule whereas the Lagrange multipliers follow $(2n + 2)$ rule for evaluation of response properties. The present research work mainly includes development of codes for CVA based FSMRCC method and implementation of these for evaluation of molecular electric properties of ionized, electron attached and electronically excited states of molecules. The organization of the thesis is as follows

We review briefly, the early developments in molecular quantum chemistry in Chapter 1. In particular, we discuss the Hartree-Fock self-consistent field method, need for introduction of electron-correlation effects. The configuration interaction theory, many-body perturbation theory will also be discussed along with the merits and demerits. The coupled cluster theory and various developments in it will be discussed in this chapter, followed by linear response method, Hellmann Feynman theorem and its applicability. Brief overview of degeneracy effects, non-dynamical correlation and formulation of MRCC methods will also be given in this chapter. At last we discuss the scope of the work done.

Chapter 2 is dedicated to ground state properties of closed shell molecules. In this chapter, we discuss the theory for closed shell systems in external magnetic field. The gauge dependence problem and some solutions to circumvent it will be briefly mentioned. We then describe formulation of ECC method for magnetic properties. At the end, we discuss the results of our implementation of ECC for obtaining ground state magnetizabilities of some small closed-shell molecules.

Chapter 3 starts with formulation of CVA-FSMRCC for one valence problem. One valence case is a complete model space problem and includes ionized (IP) and electron attached (EA) states, which basically spans doublet radicals resulting from ionization of closed-shell anions or electron-attachment to closed-shell cations. The low-lying excited states of these radicals are generally near degenerate with the ground state, which offers multi-reference character to the corresponding wave-functions. We discuss the dipole moments of some doublet radicals as test results for one-valence CVA-FSMRCCSD at the end of the chapter.

In continuation of the theory discussed in Chapter 3, we present the extension of our work to obtain second order energy derivatives in one-valence CVA-FSMRCCSD framework. We discuss the expression for second-order properties and simplification by applying $(2n + 1)$ and $(2n + 2)$ rules to cluster amplitudes, eigen vectors and Lagrange multipliers. Results for polarizabilities of the doublet radicals will be discussed at the end.

In chapter 5, we discuss CVA-FSMRCC formulation for obtaining excited state properties of molecules. Electronically excited states belong to a special type of incomplete model space, commonly referred to as quasi-complete model space. We present detailed formulation for obtaining energy derivatives in singlet and triplet excited states. Decoupling of triplet states from corresponding singlet states is also discussed. At the end, we present preliminary applications of CVA-FSMRCCSD results for obtaining dipole moment and static polarizabilities of molecules in low-lying triplet states.

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# *Chapter 1*

# A brief overview of many-body methods and Motivation of the thesis

## 1.1 Introduction

In last few decades, there have been spectacular developments in theoretical methods [1–9] to describe various chemical phenomena using principles of quantum mechanics for molecular problems introducing a branch in chemistry, the quantum chemistry. Depending on the aim of study, this can be further subdivided into two branches, namely, molecular structure [6] and molecular dynamics [10]. Although, these sub-branches focus on different aspects of chemistry, fate of the latter depends significantly, on the success of the former. It is therefore, very important to develop efficient method to accurately study the molecular structure. The failure of mean-field approaches like Hartree-Fock (HF) [6, 11–13] method in describing the electronic structure of atoms and molecules even qualitatively, demanded the development of correlated methods, commonly known as many-body methods. These include configuration interaction (CI) [6, 14, 15], many-body perturbation theory (MBPT) [16–19] and coupled-cluster (CC) [5, 20–24] methods. Since, ground state of closed-shell atoms and molecules as described by these methods involves single dominating configuration, they are collectively termed as single reference (SR) methods. Amongst these methods, the CC methods have catched special attraction because of size-consistency, size-extensivity and accurate treatment of electron-correlation effects, and have become a promising tool for molecular structure studies. Development of analytical response [25, 26] of these methods has opened up an efficient technique for obtaining energy derivatives, gradients and hessians.

The success of SR methods in explaining ground state of non-degenerate systems motivated the extension of the methods for treatment of electron-correlation effects in degenerate and near-degenerate situations, commonly referred to as quasi-degeneracy, like open-shell molecules, excited states, etc. The non-dynamical correlation effects arising from the quasi-degeneracy reflect in the dominance of more than one configurations. This resulted in the development of multi-reference (MR) methods. Analogous to SR methods, these include MRCI [27], MR-MBPT [28–31] and MRCC [7, 32–38] methods. In these methods, the dynamical correlation effects are incorporated like in the corresponding SR methods.

The separabilitity and scaling features and accuracy of SRCC methods boosted the development of MRCC methods. Mainly two approaches in MRCC enunciate effective Hamiltonian, namely, Hilbert-space (HS) MRCC [34] and Fock-space (FS) MRCC [32, 33, 37]. The state-specific MRCC [35, 36, 38] is also found to be an efficient way for treating the non-dynamical correlation effects. The linear response (LR) for effective Hamiltonian based MRCC methods has been recently formulated [39] and applied for dipole moments of open-shell radicals and excited states of molecules by Pal and co-workers [40] Hirao and co-workers [41] and Ajitha *et. al.* [42]. The Z-vector formalism

[43] in MRCC framework was also attempted. However, a more satisfactory formulation was obtained only after the extension of the constrained variational approach (CVA) of Jørgensen and Helgaker [44] in the MRCC framework. This includes the work was done in this line by Szalay [45] and independently by Pal and co-workers [46]. While the former method is applicable only for complete model spaces (CMS), the latter can be applied to general incomplete model spaces (IMS) and can be simplified for CMS and quasi-complete model spaces (QMS). Apart from these, some SR based attempts like equations-of-motion (EOM) CC [47, 48], symmetry-adapted-cluster (SAC) CI [49–54] etc. have also been there for energies and derivatives of certain quasi-degenerate cases and have become popular because of their relative simplicity.

While the SR methods are now used as a black-box tool for electronic structure calculations, due to theoretical and computational difficulties, the MR methods still continue to be developed from general applicability point of view. The present thesis aims to present some computational developments in the field of MRCC for obtaining molecular properties. In particular, we propose to present computational implementation of constrained-variational approach (CVA) introduced in FSMRCC framework for efficient evaluation of dipole moments and dipole polarizabilities of molecules in ionized, electron-attached and electronically excited states. We also present our implementation of an SRCC method for evaluating ground state magnetic properties of some closed-shell molecules. To start with, we present a brief overview of some earlier developments in many-body methods. This will help in placing relevance of the proposed work. The objective and scope of the thesis will be explained at the end.

## 1.2 Atoms and Molecules: A quantum mechanical insight

Atoms and molecules are systems containing positively charged nuclei and negatively charged electrons moving around them. Atom consists of only one nucleus. Molecules by definition will have more than one nuclei as they are formed due to stable interactions amongst a number of atoms. Except for simple systems like hydrogen atom and $H_2^+$ molecule, these contain two or more electrons. These are described by quantum mechanical bound states with various types of attractive and repulsive forces balanced within the systems. Electronic structure of atoms and molecules can be studied by solving time-independent Schrödinger wave equation [6, 8]

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

In Eq. (1.1), $\hat{H}$ is Hamiltonian operator for the total energy of the system. It is composed of kinetic energy of constituent particles, potential energy due to attractive and repulsive interactions amongst the particles and energy due to interaction of the system with the surroundings. The interactions with surroundings can be quite complicated and include the effect of external electric and/or magnetic fields, etc. In absence of external field, only the kinetic and potential energies contribute to the Hamiltonian. The kinetic energy has two parts, namely, nuclear and electronic kinetic energies respectively. The potential energy has three parts, namely, nuclear-electron attraction energy, nuclear-nuclear repulsion energy and electron-electron repulsion energy respectively. The Hamiltonian for a system of $M$ nuclei and $N$ electrons can thus be written as [6]

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

where,

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

In the above equation, $\vec{R}_A$ and $\vec{r}_i$ are spatial coordinates of $A$-th nucleus and $i$-th electron respectively and the subscripts $n$ and $e$ indicate the the entities (i.e. nuclei and electrons respectively) responsible for the corresponding interactions.

The wavefunction for $N$-electron system is a complicated function of spatial coordinates of nuclei and spatial and spin coordinates of electrons. We denote the space-spin coordinate of $i$-th electron as $\vec{x}_i = \{\vec{r}_i, \xi_i(\sigma)\}$ where $\xi_i(\sigma)$ is spin of $i$-th electron. The wavefunction $\Psi$ can thus be written as $\Psi(\vec{R}_1, \ldots, \vec{R}_M, \vec{x}_1, \ldots, \vec{x}_N)$. The wavefunction is anti-symmetric with respect to the interchange of space-spin coordinates of any two electrons.

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

It is a well-known fact that such an $N$-electron wavefunction can be expanded as a linear combination of $N$-electron anti-symmetric functions. Although an $N$-electron function can have quite complicated structure, the most convenient way is to write it as product of $N$ one-electron functions, i.e. orbitals. Anti-symmetry can be brought in by using determinant rather than simple product of the orbitals. If the orbitals form complete set, one can obtain a complete set of $N$-electron determinants and thereby, the exact wavefunction for the $N$-electron system. Another feature of the many-electron wave-function is presence of Coulomb hole and Fermi hole. Coulomb hole springs up from the coulombic repulsion amongst electrons due to which, probability of finding two electrons at the same point in space is zero. The concept of Fermi hole results from Fermi-Dirac statistics obeyed by electrons and according to this, probability of finding two electrons with parallel spin at the same point in space is zero. While an arbitrary anti-symmetric wavefunction does not ensure Coulomb hole, the anti-symmetry takes care of the Fermi hole. However, the Fermi hole also includes the corresponding Coulomb hole to some extent.

Solution of the eigenvalue problem Eq. (1.1) yields stationary state energies and the corresponding eigenfunctions. In absence of external perturbation, atoms and molecules are assumed to be in one of these states. It is however, very difficult to solve Eq. (1.1), even for small systems. Since, nuclei are much heavier than electrons, while considering electronic motions, they can virtually be assumed to be stationary. This is known as frozen-nuclei Born-Oppenheimer approximation (BOA). As a consequence of this approximation, the first term in Eq. (1.2), the kinetic energy of nuclei drops out and the inter-nuclear repulsion energy (third term in Eq. (1.2)) becomes constant. As a constant added to an operator does not affect the eigenfunctions and simply adds to the eigenvalues, effectively, the problem reduces to the solution of electronic Hamiltonian which can be written as

$$\begin{aligned}\hat{H}_{ele} &= \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \\ &= -\sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{A=1}^{M}\sum_{i=1}^{N} \frac{Z_A}{||\vec{r}_i - \vec{R}_A||} + \sum_{i=2}^{N}\sum_{j=1}^{i-1} \frac{1}{||\vec{r}_i - \vec{r}_j||} \qquad (1.5)\end{aligned}$$

The quantitative aspects including the corrections to BOA were long back addressed by Sutcliffe [55]. The eigenvalues of the electronic Hamiltonian are the total electronic energies of the corresponding stationary states. The corresponding eigenfunctions are parameterically dependent on nuclear coordinates. Addition of the inter-nuclear repulsion energy to the total electronic energy provides and effective potential energy surface (PES) $V_{\mathit{eff}}(R_1, \ldots, R_M)$ of nuclear motion. The PES resulting from different electronic states are generally well separated and the interaction between two PES is negligible. Due to this, the nuclear motions are well separated from the electronic motion. Thus, BOA turns to a very good approximation for electronic structure calculations as the problem of $M + N$ entities reduces to $N$-electron problem with fixed nuclei. The concept of PES serves to bring back chemist's view of molecules, equilibrium structure, etc. in terms of energy.

## 1.3 Theoretical model for molecular structure: Basic criteria

It may be noted that even with BO approximation, it is difficult to solve a many-electron problem because of the difficult inter-electronic repulsion term $\hat{V}_{ee}$ in the electronic Hamiltonian as defined in Eq. (1.5). The bottle-neck of quantum chemistry lies in the fact that the approximation of freezing nuclei can not be extended to the electrons. The eigenvalue problem Eq. (1.1) using the electronic Hamiltonian in Eq. (1.5) cannot be solved exactly. One has to, therefore, introduce further approximations, of course, ensuring qualitative as well as quantitative accuracy in describe the chemical phenomena. Although, 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.* [56] about forty years ago and quoted after studies and modifications by Bartlett [5] in one of his reviews, can be briefly discussed as fol1ows.

1. The method should be applicable for wide range of molecular systems. It should not be dependant on certain choices of configurations and symmetry.

2. The method should be invariant with respect to classes of transformation. In particular, the unitary transformations should not alter the orbital degeneracy and the allied effects.

3. The method should be able to properly treat dissociation of a big molecule into its fragments. This feature is known as **size-consistency**. 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 energy of a strongly interacting many-electron system for a given potential should be approximately proportional to number of electrons in the system. This scaling property is known as **size-extensivity**.

5. Even if theory is accurate in treating the electronic structure, the computational expenditure may refrain in its implementation to molecular systems of chemist's interest. Hence, the method should be cost effective and efficient.

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

Out of the above conditions, the applicability to open-shells and excited states may rather be considered as a desirable condition. For highly accurate and rigorous results, one might as well have to compromise with cost-effectivity. An ideal theoretical method must, however, obey the rest of the criteria. Size-consistency and size-extensivity are utmost important since, the efficiency and accuracy of theoretical methods are governed by these conditions.

## 1.4 Hartree-Fock theory

Amongst all the methods for obtaining approximate solutions to the electronic Schrödinger equation, Hartree-Fock (HF) theory [6, 11, 12] is the most fundamental one. It is based on the fact that stationary states, in particular, the ground states of atoms and molecules with even number of electrons can be represented by a single dominant configuration.

$$\Phi_0(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_1(\vec{x}_2) & \ldots & \chi_1(\vec{x}_N) \\ \chi_2(\vec{x}_1) & \chi_2(\vec{x}_2) & \ldots & \chi_2(\vec{x}_N) \\ \vdots & \vdots & & \vdots \\ \chi_N(\vec{x}_1) & \chi_N(\vec{x}_2) & \ldots & \chi_N(\vec{x}_N) \end{vmatrix} \tag{1.6}$$

Every electrons are assumed to be independent of each other, i.e. the electrons are assumed to move in a spherically averaged inter-electronic repulsion potential. Hence, HF is also known as independent particle model. The variation principle states that the best wavefunction of form given by Eq. (1.6) is the one, which gives the lowest possible energy.

$$E_0 =< \Phi_0|\hat{H}_{ele}|\Phi_0 > \tag{1.7}$$

The variational flexibility of the wavefunction is the choice of spin orbitals. This procedure leads to integro-differential equations referred to as HF equations, which are solved iteratively so as to make $< \Phi_0|\hat{H}_{ele}|\Phi_0 >$ stationary while keeping the orbitals orthonormal.

$$\begin{aligned} \hat{f}(\vec{x})\chi_a(\vec{x}) &= \epsilon_a \chi_a(\vec{x}) & (1.8) \\ \hat{f}(\vec{x}) &= \hat{T}_e + \hat{V}_{ne} + v_{HF}(\vec{x}) & (1.9) \\ v_{hf}(\vec{x}) &= \sum_{j=1}^{N} J_j(\vec{x}) + \sum_{j=1}^{N} K_j(\vec{x}) & (1.10) \\ J_j(\vec{x})\chi_i(\vec{x}) &= \int dx' \frac{\chi_j^*(\vec{x'})\chi_j(\vec{x'})}{|\vec{x} - \vec{x'}|} \chi_i(\vec{x}) & (1.11) \\ K_j(\vec{x})\chi_i(\vec{x}) &= \int dx' \frac{\chi_j^*(\vec{x'})\chi_i(\vec{x'})}{|\vec{x} - \vec{x'}|} \chi_j(\vec{x}) & (1.12) \end{aligned}$$

Here, the $\hat{f}(\vec{x})$ is Fock operator [6] and is an effective one-electron operator. The $v_{hf}(\vec{x})$ is average potential experienced by an electrons due to motions of all other electrons and is called HF potential. It includes the average Coulomb interaction defined by local operator $J_j(\vec{x})$ and a non-classical potential represented by a non-local operator $K_j(\vec{x})$ known as exchange potential. The exchange potential is consequence of the anti-symmetric nature of the wavefunction. The Fock operator being dependant on its eigenfunctions, the set of equations (1.8) - (1.12) are solved iteratively until some self-consistency is achieved between successive equations.

The HF procedure leads to orthonormal set of spin-orbitals, which are eigenfunctions of the Fock operator. The corresponding eigenvalues of the Fock operator are the orbital energies. The $N$ spin-orbitals with lowest energies are occupied in HF configuration and the corresponding determinant is the Hartree-Fock wavefunction. The remaining orbitals which are unoccupied in HF configuration are termed as virtual orbitals. The physical significance of orbital energies is provided by Koopmans' theorem which states that the energy of an occupied orbital in HF ground state is negative of the energy required for removing an electron from the orbital without relaxation of the rest of the orbitals. The Koopmans' theorem very accurately predicts the ionization potential because of the fact that the relaxation and correlation effects partially cancel each other. Koopmans' theorem also predicts the first electron affinity. However, these are found to be quite absurd since, the correlation and relaxation errors add up in this case.

For atoms, the HF equations can be exactly solved as integro-differential equations. For molecules, however, the explicit integration of the two-electron interaction terms is difficult as the orbitals involved are centered at different nuclei. Hence, following Roothan [13] a finite set of gaussian functions are introduced to define the spatial parts of atomic orbitals, which are then transformed to molecular orbital basis to achieve orthonormalization. For closed-shell systems, the spin-orbitals with opposite (spin-up and spin-down) spin functions are paired up and the problem can be simplified by using only spatial orbitals after spin-integration. This leads to Roothan Hall equations and the method is known as restricted HF (RHF). The open-shell systems also have most of the electrons paired up and can be solved by open-shell RHF (ROHF) method. On the other hand, this simplification of electron pairing may not be considered and one may explicitly solve the HF equations using spin-orbitals. The method is called unrestricted HF (UHF) and leads to Pople-Nesbet equations. While an RHF or ROHF determinant is a pure eigenfunction of total spin operator, UHF determinant, in general, is not.

Brillouin's theorem [6] is a result of HF theory and states that configurations obtained by excitation of a single electron from HF configuration do not directly interact with the HF configuration through Hamiltonian. This feature can be treated as defining condition of HF approximation.

The important feature of HF theory is the simplification of many-electron problem to independent particle picture by treating the electron-electron repulsion in an average way. The HF determinant recovers almost 99% of the total energy. The difference between exact energy and HF energy is called correlation energy as it arises due to partial ignorance of the electron-electron interactions. The correlation energy can be recovered by improving the approximations made in HF theory. This leads to various branches of theories collectively termed as many-body methods. However, due to the simplicity of HF theory, HF configuration is generally used as a starting guess for the many-body theories.

## 1.5 Configuration interaction method

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 specific states. Unlike for energy of stationary states, the variation principle does not hold for energy differences. These energy differences are of the order of the correlation energy. Hence, to describe these phenomena even qualitatively, it is necessary to go beyond the HF approximation and treat the electron correlation effects correctly. CI [6, 14, 15] is one of the methods to achieve this.

Conceptually, CI is the most simple method to improve the wavefunction. The fact that HF theory provides with a set of orthonormal orbitals as eigenfunctions of the Fock operator 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 will be obtained if all the configurations are included.

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 total wavefunction can thus be represented as

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

Intermediate normalization has been used in the above expansion, although, some other normalization schemes can as well be used. The $\Phi_i^a$ indicates a singly excited determinant formed by excitation of electron from $i$-th orbital (occupied) in HF determinant to the $a$-th (virtual) orbital. Similarly, $\Phi_{ij}^{ab}$ indicates doubly excited determinant obtained by exciting the electrons from $i$-th and $j$-th orbitals to $a$-th and $b$-th orbitals respectively. 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 [6]. While the lowest eigenvalue and the eigenvectors corresponds to the ground state of the system, the rest of the same correspond to excited states of the system. Alternately, the CI coefficients can also be obtained by method of projection. However, since the expression is linear in coefficients, it can be obviously proven 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) [14, 15], Davidson iterative diagonalisation [57], direct CI [58], 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) [59, 60] and symmetric group approach (SGA) [60, 61].

Except for cost-effectiveness, FCI fulfills all the criteria for a theoretical model. However, the dimensions of the wavefunctions increase rapidly with the number of electrons as well as basis functions and practically, it becomes impossible to use FCI even for small molecules with moderate size basis sets. 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 of the wavefunction, although, they can lead to excited states. Also, understanding the fact that the correlation energy originates mainly due to two-electron interactions, one must include the doubly excited configurations to improve the wavefunction. This 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. The molecular properties like dipole moments, polarizabilities, etc. are defined by one-electron operator. It is therefore, desirable to include the singly excited determinants in addition to the doubly excited ones. The method is called CI singles and doubles (CISD) and describes the one-electron properties more accurately. Although singly excited determinants do not directly mix with 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 leading to CISD and triples (CISDT), CISDT and quadrupoles (CISDTQ) and so on.

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-consistant 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 $\Psi_{AB}$ 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 [6] 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”.

## 1.6 Second quantization

As seen earlier, the determinant structure is used to ensure anti-symmetry of the wavefunction. However, this makes the equations clumsy to look at, particularly, for the many-body theories. The same algebra, without disturbing the physics of many-electron systems can be more conveniently described using the concept of second quantization. The main advantage of second quantization is replacement of the cumbersome determinant structure by ordered action of creation and annihilation operators. The consequent developments like diagrammatic techniques [62], normal ordering and Wick’s theorem [18, 62, 63] further helped in simplification of the tedious algebra and also in understanding the physics more easily. The second quantization concepts have been long back described in literature [6, 64]. In this section, we briefly mention, only some important features of second quantization which will be used in the thesis in appropriate places.

To describe second quantization, consider a complete set of orthonormal spin orbitals $\{\chi_i(x)\}$. For each spin-orbital $\chi_i$, are associated two operators $a_i^\dagger$ and $a_i$ known as creation and annihilation operators respectively. A creation operator $a_i^\dagger$ creates an electron in $\chi_i$ if it is vacant. Similarly, if $\chi_i$ is occupied, the annihilation operator $a_i$ will destroy the electron. The above mentioned effects are observed when the operators act on the right hand side. On the left hand side, the actions of the creation and annihilation operators are interchanged. A creation operator cannot create electron in an already occupied orbital. Similarly, an annihilation operator cannot destroy electron from a vacant orbital. A vacuum ($| >$ or $< |$) is defined as a state with no electrons. These results can be summarized as follows.

$$\begin{aligned}
a_i^\dagger|\chi_j(\vec{x}_1), \chi_k(\vec{x}_2), \ldots, \chi_l(\vec{x}_N) > &= |\chi_i(\vec{x}_1), \chi_j(\vec{x}_2)\chi_k(\vec{x}_3), \ldots, \chi_l(\vec{x}_{N+1}) > \\
a_i|\chi_i(\vec{x}_1), \chi_j(\vec{x}_2), \chi_k(\vec{x}_3), \ldots, \chi_l(\vec{x}_N) > &= |\chi_j(\vec{x}_1)\chi_k(\vec{x}_2), \ldots, \chi_l(\vec{x}_{N-1}) > \\
a_i^\dagger| >= |\chi_i(\vec{x}_i) > &; \quad < |a_i =< \chi_i(\vec{x}_i)| \\
a_i|\chi_i(\vec{x}_i) >= | > &; \quad < \chi_i(\vec{x}_i)|a_i^\dagger =< | \\
a_i| >= & \; 0 \quad =< |a_i^\dagger \\
a_i^\dagger|\chi_i(\vec{x}_i) >= & \; 0 \quad =< \chi_i(\vec{x}_i)|a_i
\end{aligned} \tag{1.14}$$

One can thus obtain $N$-electron determinant by action of $N$ creation operators on vacuum ($| >$). Similarly, the action of $N$ annihilation operators on vacuum on the left ($< |$) also creates $N$-electron determinant. The linear vector space spanned by determinants with different number of electrons including the vacuum is known as Fock-space [63]. It can be viewed as direct sum of Hilbert spaces with different number of electrons. The creation and annihilation operators obey following anti-commutation relations.

$$\begin{aligned}
\{a_i^\dagger, a_j^\dagger\} = & \quad a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger & = 0 \\
\{a_i, a_j\} = & \quad a_i a_j + a_j a_i & = 0 \\
\{a_i^\dagger, a_j\} = & \quad a_i^\dagger a_j + a_j a_i^\dagger & = \delta_{ij}
\end{aligned} \tag{1.15}$$

From the above relations, it can be seen that the interchange between any two creation or annihilation operators will result in change of the sign of the resulting determinant, thereby ensuring the anti-symmetry. The electronic Hamiltonian can thus be written in second quantized notation as follows.

$$\hat{H}_{ele} = \sum_{i,j} < i|\hat{h}|j > a_i^\dagger a_j + \frac{1}{2}\sum_{i,j,k,l} < ij|\hat{g}|kl > a_i^\dagger a_j^\dagger a_k a_l \tag{1.16}$$

where,

$$\begin{aligned} < i|\hat{h}|j > &= \int d\vec{x}\chi_i^*(\vec{x})\hat{h}(\vec{x})\chi_j(\vec{x}) \\ < ij|\hat{g}|kl > &= \int d\vec{x}_1 d\vec{x}_2 \chi_i^*(\vec{x}_1)\chi_j^*(\vec{x}_2)\hat{g}(||\vec{x}_1 - \vec{x}_2||)\chi_k(\vec{x}_1)\chi_l(\vec{x}_2) \end{aligned} \tag{1.17}$$

The above form of electronic Hamiltonian is independent of the number of electrons and can be applied to the whole of Fock-space.

### 1.6.1 Normal-ordered operators and Wick's theorem

It is clear from Eq. (1.14), that action of annihilation operator on vacuum is zero. Hence, following Eq. (1.15), one can rearrange the creation and annihilation operators such that, all the annihilation operators are shifted to the right hand side. This process is called normal ordering [62, 63]. A sequence of the creation and annihilation operators said to be normal-ordered if all the annihilation operators precede the creation operators. The interchange between any two creation or annihilation operators changes only the sign of the operator. The interchange between a creation and an annihilation operator generates two terms. The term not containing the pair of creation-annihilation operators is known as contraction term. The pair of creation-annihilation operators are said to be contracted in this term.

The normal ordering process simplifies the evaluation of matrix elements of operators. Since vacuum expectation value is zero, the matrix element of an operator will survive only when all the creation and annihilation operators are fully contracted with each other. The process is simplified by applying Wick's theorem [18, 62, 63], which states that any general operator sequence is equal to the sum of its normal-ordered form and normal-ordered forms of its all possible contractions. The generalized form of the theorem says that product of two normal-ordered operators is equal to sum of the normal-ordered form of the product and normal-ordered forms of all possible contractions between the two operators except self-contractions.

The second quantized algebra can be solved graphically. A second quantized operator is represented graphically by a vertex. The creation and annihilation operators are represented by the outgoing and incoming lines originated at the vertex. A line joining two vertices (i.e. two operators) is termed as internal line and represents a contraction between the corresponding operators.

### 1.6.2 Hole-Particle definition

The second-quantized algebra can be more easily solved, if instead of absolute occupancy, the occupancy with respect to some reference configuration is considered. This results in replacement of electrons by new entities, namely, holes and particles. We define a hole as absence of an electron in an orbital occupied in the reference configuration. Conversely, particle is defined as presence of electron in a orbital not occupied in reference configuration. In terms of holes and particles, the reference configuration is empty physically, it contains the electrons. It is therefore termed as hole-particle vacuum.

The normal-ordering concept and Wick's theorem can be extended to the hole-particle operators easily. When normal-ordered with respect to the HF vacuum, the electronic Hamiltonian can be written as

$$\hat{H}_{ele} = \hat{H}_{vac} + \hat{H}_N \tag{1.18}$$

where,

$$\begin{aligned}
\hat{H}_{vac} &= <\Phi_0|\hat{H}_{ele}|\Phi_0>; \\
\hat{H}_N &= \sum_{i,j} <i|\hat{u}|j> a_i^\dagger a_j + \frac{1}{2}\sum_{i,j,k,l} <ij|\hat{g}|kl> a_i^\dagger a_j^\dagger a_k a_l \\
<i|\hat{u}|j> &= <i|\hat{h}|j> + \sum_{a\in\Phi_0}\{<ia|\hat{g}|ja> - <ia|\hat{g}|aj>\} \qquad (1.19)
\end{aligned}$$

The $\hat{H}_{vac}$ in case of HF vacuum gives the HF energy. Consequently, the normal-ordered electronic Hamiltonian ($\hat{H}_N$) will directly give the correlation energy. The hole-particle algebra can also be solved using graphical representation. A hole is denoted by a line with a downward arrow. An upward arrow stands for particle. The graphical representation of a operator in terms of holes and particles can be defined as follows. The hole creation and annihilation are denoted by incoming and outgoing lines with downward arrows. Similarly, creation and annihilation of particle can be denoted by outgoing and incoming lines with upward arrow respectively. Analogous to the fermion-based second quantized algebra, the contraction between two operators is represented by a common line joining the two operators, also known as internal line. In hole-particle context, the internal line can either be hole line or a particle line.

To illustrate the hole-particle concept let us consider example of CI. If we consider HF configuration as hole-particle vacuum, singly excited determinants will contain a hole and a particle, doubly excited determinants will contain two of each, and so on. In other words, excitation of an electron from reference determinant by excitation operator leads to creation of a hole and a particle.

## 1.7 Many body perturbation theory

MBPT [16–18] is one amongst the most popular and widely used correlated method. The method offers a systematic procedure to step by step incorporate the dynamical correlation effects.

In MBPT, the electronic Hamiltonian is partitioned into two part. One of them is the known part and is the dominant one. It is termed as zeroth order Hamiltonian denoted by $\hat{H}_0$. 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 $< \Psi_i^0|V|\Psi_j^0 >$ are assumed to be known. Depending on the way, the partitioning is done, there are two variants, namely Møller-Plessette (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 $\lambda$ in the definition of exact Hamiltonian, which is smoothly varied from $0$ to $1$.

$$\hat{H} = \hat{H}_0 + \lambda V \tag{1.20}$$

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 $\lambda = 0$.

$$\begin{aligned} \Psi_i &= \Psi_i^0 + \lambda \Psi_i^1 + \frac{\lambda^2}{2!}\Psi_i^2 + \frac{\lambda^3}{3!}\Psi_i^3 + \ldots \\ E_i &= E_i^0 + \lambda E_i^1 + \frac{\lambda^2}{2!}E_i^2 + \frac{\lambda^3}{3!}E_i^3 + \ldots \end{aligned} \tag{1.21}$$

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) [18] and the other one developed by Rayleigh and Schrödinger known as Rayleigh-Schrödinger perturbation theory (RSPT) [16, 18, 19]. 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. (1.20) and Eq. (1.21), are substituted in the Schrödinger equation. The terms with fixed power of $V$ are then collected together and solved for energies and wavefunctions at various orders. It can be seen that, RSPT with MP partitioning leads to a size-extensive perturbation series. This feature was first proven by Brueckner [65] for first few orders in the context of infinite nuclear matter. However, he couldn't prove it for higher orders. Goldstone [66] 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 [67] 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 caliberated 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.

## 1.8 Coupled-cluster theory

Amongst the electron-correlation theories known so far, CC methods (CCM) [5, 20–23] are the most accurate ones. Endowed with meritorious features from a wide range of theories like CI [6, 14, 15], pair theories [2, 68], MBPT [16–18], etc. CCM have become methods of choice for electronic structure calculations of atoms and molecules. 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 CCM are collectively known as SRCC. If a quantity $A$ associated with an $N$-particle system is additively separable, it can be shown that $\mathbf{e}^A$ is multiplicatively separable. Further, as has been shown in the context of thermodynamics for free energy [69], $A$ must have contributions only from linked cluster to establish additive separability. This cumulative expansion of the exponential wave-operator also known as Ursell and Meyer [70] expansion was first introduced by Coester and Kummel [71] in nuclear physics.

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.

$$|\Psi_0 >= \mathbf{e}^T |\Phi_0 > \tag{1.22}$$

Usually, the intermediate normalization scheme $< \Phi_0|\Phi_0 >= 1 =< \Phi_0|\Psi_0 >$ 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.

$$T = T_1 + T_2 + \ldots + T_N \tag{1.23}$$

with

$$\begin{aligned} T_1 &= \sum_{i\in occ}\sum_{a\in virt} t_i^a\{a_a^\dagger a_i\} \\ T_2 &= \sum_{i,j\in occ}\sum_{a,b\in virt} t_{ij}^{ab}\{a_a^\dagger a_b^\dagger a_j a_i\} \\ &\text{and so on.} \end{aligned} \tag{1.24}$$

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.

$$\begin{aligned} C_1 &= T_1 \\ C_2 &= T_2 + \frac{1}{2!}T_1^2 \\ C_3 &= T_3 + T_1T_2 + \frac{1}{3!}T_1^3 \\ C_4 &= T_4 + T_1T_3 + \frac{1}{2!}T_1^2T_2 + \frac{1}{2!}T_2^2 + \frac{1}{4!}T_1^4 \\ &\text{and so on.} \end{aligned} \tag{1.25}$$

Above relationship between $T$ and $C$ is however, not valid in case of truncated CI and CC methods. Using the definition of $\Psi$ given in Eq. (1.22), one can write the Schrödinger equation with normal-ordered Hamiltonian as

$$\hat{H}_N \mathbf{e}^T|\Phi_0 >= E_0^{corr}\mathbf{e}^T|\Phi_0 > \tag{1.26}$$

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 anasatz. A traditional CC anasatz, 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. (1.26) 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. (1.26) by $\mathbf{e}^{-T}$ to obtain

$$\mathbf{e}^{-T}\hat{H}_N\mathbf{e}^{T}|\Phi_0>= E_0^{corr}|\Phi_0> \tag{1.27}$$

Using the Campbell-Baker-Hausdorff formula for $\mathbf{e}^{-A}B\mathbf{e}^{A}$, the similarity transformed Hamiltonian $\tilde{H}$ can be written as

$$\tilde{H} = \hat{H}_N + [\hat{H}_N, T] + \frac{1}{2!}[[\hat{H}_N, T], T] + \frac{1}{3!}[[[\hat{H}_N, T], T], T] + \dots \tag{1.28}$$

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

$$\mathbf{e}^{-T}\hat{H}_N\mathbf{e}^{T} = (\hat{H}_N\mathbf{e}^{T})_C \tag{1.29}$$

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. (1.29) can be shown to terminate after the quartic power of $T$. The left hand side of Eq. (1.29) 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 and can, in principle, have complex eigenvalues. However, unlike CI, the energy solution in CC framework no more remains an eigenvalue problem. The ground state correlation energy can be obtained as $\Phi_0$ expectation value of $\tilde{H}$. However, this procedure is valid only for ground state calculations. Thus, the non-hermiticity of CC anasatz does not create any inadequacies as far as we are interested in the ground state of the system. The equations for for $I$-body cluster amplitudes are obtained by equating the $\tilde{H}$ matrix elements of $I$-tuply excited configurations $\Phi I$ and the HF configuration to zero.

$$E_0^{corr} =< \Phi_0|\tilde{H}|\Phi_0 >=< \Phi_0|(\hat{H}_N\mathbf{e}^T)_C|\Phi_0 > \tag{1.30}$$

and

$$0 =< \Phi_I|\tilde{H}|\Phi_0 >=< \Phi_I|(\hat{H}_N\mathbf{e}^T)_C|\Phi_0 > \tag{1.31}$$

The Eq. (1.31) 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. (1.30).

If the $T$ as defined in Eq. (1.23) is used; the method is known as full CC (FCC) and 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 anasatz 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 and size-extensive. This is because of the exponential nature of the wave operator, which includes higher excitations through the products of $T_1$ and $T_2$. The CCSD anasatz can be further improved by perturbative or complete inclusion of triples, (CCSD(T) and CCSDT) [21, 22], quadrupoles (CCSDT(Q) and CCSDTQ) [23], etc. These anasatz are seen to further accelerate the convergence the results towards the exactness.

Non-linearity of CC equation and non-variational nature are the only limitations of the method. However, the gives highly accurate and systematically improving results during every iterative steps even when truncated. The exponential nature of the wave-operator and the connectedness of the terms ensure the size-consistency and size-extensivity of the anasatz.

## 1.9 Alternate SRCC approaches

As mentioned in 1.8, the Eq. (1.26) can be solved in various ways. We have seen that NCC is a non-variational method. Although, the proof of size-extensivity is transparent in NCC, the non-variational nature makes it computationally unattractive for energy derivatives, as will be discussed later in this chapter. Alternately, CC wavefunction (Eq. (1.22)) may be solved variationally. General advantage of stationary CCM is applicability of Hellmann-Feynman theorem and existence of $(2n + 1)$ rule for energy derivative calculations. There have been different methods for variational solutions of CC wavefunction leading to different SRCC anasatz. We briefly discuss them here.

### 1.9.1 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 $< \Psi_0^*|\hat{H}|\Psi_0 > / < \Psi_0^*|\Psi_0 >$. It follows

$$E = \frac{< \Phi_0|\mathbf{e}^{T^\dagger}\hat{H}\mathbf{e}^{T}|\Phi_0 >}{< \Phi_0|\mathbf{e}^{T^\dagger}\mathbf{e}^{T}|\Phi_0 >} \tag{1.32}$$

While $T$ operators are hole-particle creation operators like in NCC; the $T^\dagger$ being conjugate of $T$, indicate hole-particle destruction.

$$T^\dagger = T_1^\dagger + T_2^\dagger + \ldots + T_N^\dagger \tag{1.33}$$

where,

$$\begin{aligned} T_1^\dagger &= \sum_{i\in occ}\sum_{a\in virt} t_a^i\{a_i^\dagger a_a\} \\ T_2^\dagger &= \sum_{i,j\in occ}\sum_{a,b\in virt} t_{ab}^{ij}\{a_i^\dagger a_j^\dagger a_b a_a\} \\ &\text{and so on.} \end{aligned} \tag{1.34}$$

The functional in Eq. (1.32) was named as expectation value CC (XCC) [72–74]. Although, the series given in Eq. (1.32) contains some disconnected terms, it was shown by Pal *et. al.* [72] that the disconnected part of the numerator is exactly cancelled by the denominator leaving behind a completely connected series.

$$E =< \Phi_0|\mathbf{e}^{T^\dagger} H \mathbf{e}^T|\Phi_0 >_C \tag{1.35}$$

However, the cancellation implicitly implies complete expansion of the power series of the numerator and denominator of Eq. (1.32) in terms of the cluster amplitudes. The cluster amplitudes are obtained by making the energy functional (Eq. 1.35) 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.* [73] 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 [74] 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 1.7) 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 [75] and Primas [76], Kutzelnigg [77] proposed an alternate approach in variational CCM called unitary CC (UCC). The functional is given by

$$|\Psi_0 >= \mathbf{e}^{\sigma}|\Phi_0 > \tag{1.36}$$

where $\sigma$ is anti-hermitian. The special choice of $\sigma$ may be $\sigma = T - T^{\dagger}$. The cluster amplitudes may be obtained using variational or non-variational amplitudes. The non-variational [78] approach is somewhat similar to NCC where, the set of equations can be obtained by replacing the $T$ in the NCC equations by $\sigma$.

Conversely, UCC may be solved variationally as suggested by Kutzelnigg [77]. The expectation value like UCC functional can be written as

$$E = \frac{< \Phi_0|\mathbf{e}^{-\sigma}\hat{H}\mathbf{e}^{\sigma}|\Phi_0 >}{< \Phi_0|\mathbf{e}^{-\sigma}\mathbf{e}^{\sigma}|\Phi_0 >} \tag{1.37}$$

The denominator taken to all orders is identically equal to unity. This leads to a similarity transformed functional like NCC. However, the $\sigma$ amplitudes are obtained variationally like in XCC. Bartlett and Noga used UCC(n) anasatz [79] analogous to XCC(n). However, unlike XCC(n), UCC(n) functional is symmetric.

### 1.9.2 Extended coupled-cluster method

As seen earlier, similarity transformed form of NCC anasatz given by Eq. (1.27) turns out to be a compact tool for developing algorithms for ground state energy. Arponen [80] extended this feature by adding one more similarity transformation on the Hamiltonian using hole particle destruction operators.

$$E_0^{corr} =< \Phi_0|\mathbf{e}^{S}\mathbf{e}^{-\tau}\hat{H}_N\mathbf{e}^{\tau}\text{-}\mathbf{S}|\Psi_0 > \tag{1.38}$$

The resulting anasatz was named as extended CC (ECC) [81–86]. In the above equation, the $\tau$ 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 $\tau$. A transformation on $\tau$ deals with new set of hole-particle creation operators $T$ which absorb full contractions of $S$ operators with singular $\tau$ operator. This leads to a double linked energy functional.

$$E_0^{corr} =< \Phi_0|\mathbf{e}^S[\hat{H}_N\mathbf{e}^T]_L|\Psi_0 >_{DL} \tag{1.39}$$

The subscript $L$ indicates direct linking of $T$ with $\hat{H}$. The subscript $DL$ implies a 'double' or 'defined' linking [81] resulting from the transformation of $\tau$ 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 [87].

Various features of ECC will be discussed in detail in the next chapter along with its applications for obtaining magnetizabilities of closed-shell molecules.

## 1.10 Linear response method for molecular properties

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

$$\hat{H}(g) = \hat{H}^{(0)} + g\hat{O} \tag{1.40}$$

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

$$\Upsilon(g) = \sum_k \frac{1}{k!} g^k \Upsilon^{(k)} \tag{1.41}$$

In above equation, the $\Upsilon^{(k)}$ reads $k$-th order derivative of $\Upsilon$ 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 approach and requires very accurate evaluation of wavefunction and energy, although, no computational developments are required. Alternately, the molecular properties may be obtained analytically. In analytical method, explicit expressions for wavefunction derivatives are solved and used to obtain molecular properties. It is known that an exact wavefunction follows Hellmann-Feynman theorem.

$$\frac{\partial}{\partial g} \int \Psi(g) \hat{A}(g) \Psi(g) d\tau = \int \Psi(g) \frac{\partial \hat{A}}{\partial g} \Psi(g) d\tau \tag{1.42}$$

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 response properties up to $(2n+1)$-th order. This is the famous $(2n+1)$-rule used in the context of analytical response properties. For a general non-exact 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-Feynmann theorem. Hence, in electronic structure theories, emphasis is given on stationarity of the wavefunctions.

### 1.10.1 NCC linear response

The NCC-LR was initiated by Monkhorst [25]. In presence of a uniform external field, the NCC wavefunction can be expanded in Taylor series of $g$ as given in Eq. (1.41). The expressions for derivatives of energy and wavefunctions are obtained by differentiating Eq. (1.30) and Eq. (1.31) 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.

$$E_0^{corr(1)} = < \Phi_0|[(\hat{O}\mathbf{e}^T)_C + (\hat{H}_N\mathbf{e}^T T^{(1)})_C]|\Phi_0 > \tag{1.43}$$

$$0 = < \Phi_I|[(\hat{O}\mathbf{e}^T)_C + (\hat{H}_N\mathbf{e}^T T^{(1)})_C]|\Phi_0 > \tag{1.44}$$

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.

### 1.10.2 Cost-effective techniques in analytical NCC-LR

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 [88], Bartlett and co-workers [26, 89, 90] introduced the Z-vector technique in NCC-LR. The idea was taken from Handy and Schaefer [91] who used the technique for analytical derivatives for CI method. We rewrite Eq. (1.43) and Eq. (1.44) in a compact form as

$$\begin{aligned} E_0^{corr(1)} &= Y^T T^{(1)} + Q(\hat{O}) && (1.45) \\ 0 &= A T^{(1)} + B(\hat{O}) && (1.46) \end{aligned}$$

where,

$$\begin{aligned} Y^T T^{(1)} &= <\Phi_0|(\hat{H}_N \mathbf{e}^T T^{(1)})_C|\Phi_0> \quad ; \quad Q(\hat{O}) = <\Phi_0|(\hat{O}\mathbf{e}^T)_C|\Phi_0> \\ A T^{(1)} &= <\Phi_I|(\hat{H}_N \mathbf{e}^T T^{(1)})_C|\Phi_0> \quad \text{and} \quad B(\hat{O}) = <\Phi_I|(\hat{O}\mathbf{e}^T)_C|\Phi_0> \quad (1.47) \end{aligned}$$

We introduce a perturbation independent vector $Z^T$ as

$$Z^T A = Y^T \tag{1.48}$$

Following Eq. (1.48) and Eq. (1.46) and substituting them into Eq. (1.45), it follows,

$$E_0^{corr(1)} = Z^T B(\hat{O}) + Q(\hat{O}) \tag{1.49}$$

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. (1.48), 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 [44, 92, 93] 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.

$$\Im(\Upsilon) =< \Phi_0|(\hat{H}\mathbf{e}^T)_C|\Phi_0 > + \sum_{I\neq 0} \lambda_I < \Phi_I|(\hat{H}\mathbf{e}^T)_C|\Phi_0 > \tag{1.50}$$

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 $\lambda$ are optimized with the cluster equations as the constraint. The optimization of $\Im$ leads to equations for $\lambda$-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 $\lambda$-vectors follow $(2n + 2)$-rule [92, 93].

### 1.10.3 Linear response to stationary CC anasatz

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 [94] and extensively used for obtaining static properties [95–97] 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 [95, 96] 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 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 [98].

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 [84, 85]. Recently, we have attempted to use ECC for obtaining magnetic properties [86], which will be discussed in details in the next chapter.

## 1.11 Quasi-degeneracy and non-dynamical electron-correlation

The SR methods provide good description of many-electron systems with single dominant configuration termed as reference configuration. These include ground states of closed-shell atoms and molecules and some open-shell systems describable by single dominant UHF or ROHF configuration. The electron-correlation introduced by SR methods is due to weak interactions between the reference configuration and the remaining configurations arising due to electron-electron repulsions and is known as dynamical electron-correlation. However, in chemistry one often comes across quasi-degenerate situations like bond-dissociation, ionization, electronic excitations, electron-attachment, etc. where more than one configurations are seen to make dominant configurations to the wavefunction of the system. These dominant configurations interact more strongly amongst themselves than with the other configurations. These strong interactions, as a result of quasi-degeneracy of the corresponding exact states, lead to what is termed as non-dynamical electron-correlation. Such situations can not simply be described by SR methods because the non-dynamical correlation effects are much bigger in magnitude as compared to the dynamical electron-correlation. One has to therefore look for theories which introduce the non-dynamical correlation effects in addition to the features offered by the SR theories.

Important features of some of the methods well-known for dealing with quasi-degenerate situations are briefly discussed here. Some of these are suitable for “energy-of-states” calculations whereas, the others are used for “difference energy” calculations.

### 1.11.1 Multi-reference configuration interaction method

MRCI [27, 99–102] is one of the standard benchmark methods in quantum chemistry. It is a straightforward extension of the SRCI method and has been a popular tool in molecular spectroscopy. In this method, the reference function is taken as linear combination of several strongly interacting dominant configurations, known as model space. The dynamical correlation is brought in by carrying out excitations on each determinant in the model space through a linear wave-operator. Like SRCI, the truncated forms of MRCI also lack size-extensivity. Several attempts to reduce this drawback have lead to a number of methods commonly known as MR coupled-electron-pair approximation (CEPA) methods [103–105].

### 1.11.2 Multi-reference perturbation theories

The multi-reference perturbation theory (MRPT) [28, 29] closely resembles with the MBPT theory except for the MR character of the model space. A zeroth order wave-function 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) [30, 31]. 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.

### 1.11.3 Equations-of-motion methods

The EOM methods provide a compact tool to obtain difference energies directly rather than evaluating total energies of different states. In these method, Rowe's [106] equation is solved for excitation operator $Q^\dagger(K)$ given by

$$Q^\dagger(K)|\Psi_0^U >= |\Psi_K^W > \tag{1.51}$$

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 $|\Psi_0^N >$ 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 $|\Psi_0^N>$.

$$|\Psi_K^{N+1}>= Q^\dagger(K)|\Psi_0^N> \tag{1.52}$$

where,

$$Q^\dagger(K) = \sum_l t(K,l)T^\dagger(l) \tag{1.53}$$

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 $\chi_a$, operators $\{a_a^\dagger a_b^\dagger a_i\}$ which add an electron to orbital $\chi_a$ and excite another electron from $\chi_i$ to $\chi_b$, operators $\{a_a^\dagger a_b^\dagger a_c^\dagger a_j a_i\}$ which, in addition to adding electron in orbital $\chi_a$ excite electrons from orbitals $\chi_i$ and $\chi_j$ to the orbitals $\chi_b$ and $\chi_c$ respectively, and so on. Both the systems satisfy the Schrödinger equation.

$$\hat{H}|\Psi_0^N> \;=\; E_0^N|\Psi_0^N> \tag{1.54}$$

$$\hat{H}|\Psi_K^{N+1}> \;=\; E_K^{N+1}|\Psi_K^{N+1}> \tag{1.55}$$

The operator $\hat{H}$ is as defined by Eq. (1.16). Following Eq. (1.52), Eq. (1.54) and Eq. (1.55), one can easily show that

$$[\hat{H}, Q^\dagger(K)]|\Psi_0^N>= (\hat{H}Q^\dagger(K) - Q^\dagger(K)\hat{H})|\Psi_0^N>= (E_K^{N+1} - E_0^N)Q^\dagger(K)|\Psi_0^N> \tag{1.56}$$

The Eq. (1.56) 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 $|\Psi_0^N>$ 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” [107]. Simons *et. al.* used Møller-Plessette (MP) [108] expansion for the wavefunction. The EOM approach using CC anasatz led to the EOM-CC [47, 109–113] 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.

### 1.11.4 Multi-reference CC methods

The spectacular success of SRCC in accurate description of electronic structure of non-degenerate ground states of molecules boosted the extension of the methods for handling quasi-degenerate situations. The attempts in this direction led to a bunch of CCM collectively known as MRCC [7, 32–37, 39, 114–116]. Out of these, the functionals which articulate effective Hamiltonian have been extensively studied since last few years. Depending on the way the MR character is brought in, these furcate into state universal (SU) or HSMRCC [34] and valence universal (VU) or FSMRCC [32, 33, 37, 39, 114–116]. While the former uses different vacua for different configurations in the model space, the latter is based on the concept of common vacuum. Both these methods suffer from the so called intruder state problem. However, this problem can be eliminated by use of IMS or QMS. Methods based on use of intermediate Hamiltonian or more recently, the state-specific MRCC methods [35, 36] are also known to circumvent this problem. All these method have different territories of applicability due to pros and cons inherent in their structure. In the present thesis, computational developments in constrained variational response to FSMRCC are major part of the research. Therefore, we now focus on the features of FSMRCC from the view point of CVA formulation.

## 1.12 Fock-space multi-reference coupled-cluster method

As mentioned earlier, FSMRCC [32, 33, 39, 114–116] 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

$$|\Psi_\mu^{(p,h)}>=\sum_i C_{i\mu}^{(p,h)}|\Phi_i^{(p,h)}> \tag{1.57}$$

The projection operator for model space is defined as

$$P^{(p,h)}=\sum_i |\Phi_i^{(p,h)}><\Phi_i^{(p,h)}| \tag{1.58}$$

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

$$Q = 1 - P \tag{1.59}$$

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 $\Omega$ 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, $\Omega$ should contain cluster operators $\{\tilde{T}^{(p,h)}\}$ which are defined as follows

$$\tilde{T}^{(p,h)}=\sum_{k=0}^{p}\sum_{l=0}^{h} T^{(k,l)} \tag{1.60}$$

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 $\Omega$ is defined as follows.

$$\Omega = \{e^{\tilde{T}^{(p,h)}}\} \tag{1.61}$$

The brace-bracket in Eq. (1.61) indicates normal ordering of the cluster-operators. The Schrödinger equation for the manifold of quasi-degenerate states can be written as

$$\begin{aligned} H|\Psi_i^{(p,h)}> &= E_i|\Psi_i^{(p,h)}> \\ &\text{which leads to} \\ H\Omega(\sum_i C_{i\mu}^{(p,h)}\Phi_i^{(p,h)}) &= E_\mu\Omega(\sum_i C_{i\mu}^{(p,h)}\Phi_i^{(p,h)}) \qquad (1.62) \end{aligned}$$

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

$$\sum_j (H_{\mathit{eff}}^{(p,h)})_{ij} C_{j\mu} = E_\mu C_{i\mu} \tag{1.63}$$

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

which can be written as

$$H_{\mathit{eff}}^{(p,h)} = P^{(p,h)}\Omega^{-1}H\Omega P^{(p,h)} \tag{1.64}$$

The form the inverse of $\Omega$, in general may not be well defined. Hence, above definition is seldom used to obtain the effective Hamiltonian. Instead, the Bloch-Lindgren approach is commonly used to define the effective Hamiltonian. The Bloch equation is just a modified form of Schrödinger equation.

$$H\Omega P = \Omega H_{\mathit{eff}} P \tag{1.65}$$

The Bloch-Lindgren approach not only eliminates the requirement of $\Omega^{-1}$, 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

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

$$\begin{aligned} P^{(k,l)}[H\Omega - \Omega H_{\mathit{eff}}^{(k,l)}]P^{(k,l)} &= 0 \\ Q^{(k,l)}[H\Omega - \Omega H_{\mathit{eff}}^{(k,l)}]P^{(k,l)} &= 0 \\ &;\forall k = 0, \ldots, p; l = 0, \ldots, h \end{aligned} \tag{1.66}$$

The normalization condition is specified indirectly through parameterization of $\Omega$. 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.

$$H_{\mathit{eff}}^{(p,h)} C^{(p,h)} = C^{(p,h)} E$$

$$\tilde{C}^{(p,h)} H_{\mathit{eff}}^{(p,h)} = E \tilde{C}^{(p,h)} \tag{1.67}$$

$$\tilde{C}^{(p,h)} C^{(p,h)} = C^{(p,h)} \tilde{C}^{(p,h)} = 1 \tag{1.68}$$

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. The LR in FSMRCC framework was initiated by Pal [39] and then implemented by Pal and co-workers [40] 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 $\Upsilon = \{H_{\mathit{eff}}^{(p,h)}, C^{(p,h)}, \tilde{C}^{(p,h)}, E, \Omega\}$ become perturbation dependent and can be expanded in Taylor series of $g$.

$$\Upsilon(g) = \Upsilon^{(0)} + g\Upsilon^{(1)} + \frac{1}{2!}g^2\Upsilon^{(2)} + \frac{1}{3!}g^3\Upsilon^{(3)} + \dots \tag{1.69}$$

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 $\Omega$ 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.

$$\sum_i \{(H_{\mathit{eff}}^{(1)})_{ji} C_{i\mu}^{(0)} + (H_{\mathit{eff}}^{(0)})_{ji} C_{i\mu}^{(1)}\} = E_\mu^{(1)} C_{j\mu}^{(0)} + E_\mu^{(0)} C_{j\mu}^{(1)} \tag{1.70}$$

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 [43] is one of them. Szalay [45] formulated the CVA technique in FSMRCC but the method was applicable only for CMS. Later, Pal and co-workers [46] independently formulated the CVA-FSMRCC for general IMS and showed that the functional simplifies to the one proposed by Szalay [45] if applied for CMS and QMS. The CVA-FSMRCC method of Pal an 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

$$E_\mu = \sum_{ij} \tilde{C}^{(p,h)}_{\mu i} (H_{\textit{eff}})^{(p,h)}_{ij} C^{(p,h)}_{j\mu} \tag{1.71}$$

We construct the Lagrangian to minimize the energy expression given above, with the constraint that the MRCC equations [Eq. (1.66)] are satisfied for the state $\mu$.

$$\begin{aligned} \Im \;=\; & \sum_{ij} \tilde{C}^{(p,h)}_{\mu i} (H_{\textit{eff}})^{(p,h)}_{ij} C^{(p,h)}_{j\mu} \\ & + \sum_{k=0}^{p} \sum_{l=0}^{h} \{ P^{(k,l)} \Lambda^{(k,l)} P^{(k,l)} P^{(k,l)} [H\Omega - \Omega H^{(k,l)}_{\textit{eff}}] P^{(k,l)} \\ & + P^{(k,l)} \Lambda^{(k,l)} Q^{(k,l)} Q^{(k,l)} [H\Omega - \Omega H^{(k,l)}_{\textit{eff}}] P^{(k,l)} \} \\ & + E_\mu [\sum_{ij} \tilde{C}^{(p,h)}_{\mu i} C^{(p,h)}_{j\mu} - 1] \end{aligned} \tag{1.72}$$

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. (1.72) and the finer details regarding simplifications in certain cases will be discussed in appropriate places.

## 1.13 Objectives of the thesis

Due to efficient techniques available for obtaining energy derivatives, SRCC methods are now very commonly used for evaluation of molecular electric properties like dipole moment, polarizabilities, hyperpolarizabilities, etc. However, there have been much fewer implementations of these methods for obtaining magnetic properties. The extention of CCM for magnetic properties is non-trivial due to the so called gauge-dependence problem and complex nature of the perturbation. This fact motivated two lines of research, namely, to introduce techniques for elimination of gauge-dependence and indoctrinate them in efficient SRCC methods. Recognizing the advantages of stationary nature of ECC, we attempt to use ECCSD method for obtaining ground state magnetizabilities of some closed-shell molecules, which are presented in Chapter 2. The effect of external uniform magnetic field on molecular Hamiltonian, gauge-dependence problem in magnetic properties and solutions to circumvent the problem are also discussed. Some pilot applications of obtaining magnetizabilities of molecules using moderate sized basis sets are presented.

Although, large number of methods are available for ground state properties of closed-shell molecules, there have been very few developments for efficient evaluation of particularly, higher order response properties of molecules in quasi-degenerate situations like ionized, electron-attached and electronically excited states. We present the pilot applications for these cases using our computational developments of CVA-FSMRCCSD. In Chapter 3, we present dipole moments of doublet radicals in ground states and low-lying excited states using CVA-FSMRCCSD. These radicals can be viewed as ionized states of closed-shell anions or electron-attached states of closed-shell cations resembling to $(0, 1)$ and $(1, 0)$ sectors of Fock-space respectively. We present the analytical static polarizabilites of these systems in Chapter 4. Chapter 5 is dedicated to excited state electric properties of molecules. We discuss the CVA formalism for $(1, 1)$ FS sector problem and decoupling scheme between the singlet and triplet states. At last we present some pilot applications of CVA-FSMRCCSD and present analytical dipole moments and polarizabilities of some small molecules in low-lying triplet states. The results presented in this chapter are preliminary and we would eventually like to extend and apply the method for more difficult cases like singlet excited states of molecules.

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# *Chapter 2*

# Ground state magnetizabilities of some closed-shell molecules

## 2.1 Introduction

In past few years, evaluation of magnetic properties has been one of the important and challenging areas for theoretical chemists. The developments of spectroscopic techniques like nuclear magnetic resonance (NMR) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, etc. demanded the accuracy in obtaining these properties. Although, theoretically, magnetic properties are obtained by extension of linear response methods used for electric properties, practically, the procedure of calculating these properties is quite complicated. The complex nature of magnetic field is one of the problems. The problem can, however, be eliminated for analytical methods by working out the complex algebra to obtain simplified real algebra for evaluating the magnetic properties. Another problem is the dependence of the magnetic properties on the choice of gauge origin [1].

The magnetic response studies thus involve two steps. The first step is to extend the efficient response techniques in correlated methods [2–5] for magnetic properties. The other line of research was to design a procedure to eliminate the so called gauge dependence problem. This led to development of tools like use of gauge-including atomic orbitals (GIAO) [6–15], individual gauge for localized orbitals (IGLO) [1, 16], polarization propagator approach (PPA) [17], local origin (LORG) methods [18], random phase approximation (RPA), etc. Depending on the desired accuracy, the suitable technique may be used for calculations.

All these techniques have now been incorporated well in the methods like HF [19–21], MBPT [11, 15, 22], etc. The CVA, based on the method of Lagrange undetermined multipliers, has also made it plausible to extend these techniques in sophisticated method like CCM [23–26]. However, a more sophisticated way is to use ECC [5, 27] anasatz. The advantages of ECC over NCC method were recently addressed by Piecuch and co-workers [28]. The double-similarity transformed structure of the ECC energy functional brings in the higher order perturbative corrections due to exponential nature of the left vectors in contrast to the CVA-NCC method where, the left vectors are linear in nature. Thus, ECC is perturbatively much superior than NCC and it is therefore, desirable to use ECC for analytical response properties. ECC has been extensively used for energy [29] and electric properties [30, 31]. In this chapter, we present our attempt of obtaining magnetizabilities of some closed shell molecules using ECCSD method. Although, we have not incorporated the gauge invariance techniques in our method, this attempt is a step towards indoctrination of these techniques in ECC. We discuss the effect of external uniform magnetic field on Hamiltonian of the molecular system in the next section. This will be followed by description of ECC method. At the end, we present the ground state magnetizabilities of hydrogen fluoride and carbon monoxide obtained using some moderate size basis-sets.

## 2.2 Molecule in a uniform external magnetic field

In absence of external magnetic field, the electronic Hamiltonian of a molecule in atomic units is given by

$$\hat{H}^0 = \frac{p^2}{2} + V \tag{2.1}$$

The above equation is just a compact form of Eq. (1.2). In presence of an external magnetic field $\vec{B}$, the Hamiltonian of the system is not uniquely defined [1], but depends on the gauge origin $\vec{R}_G$ for which, any location can be chosen. If $\mu_{nuc}$ reads magnetic moment of nucleus located at $\vec{R}_N$, then in atomic units, the Hamiltonian [16] of the system can be written as

$$\begin{aligned}\hat{H} &= \hat{H}^0 + \frac{1}{2c}[(\vec{r} - \vec{R}_G) \times \vec{p}] \bullet \vec{B} + \frac{1}{c}\frac{[(\vec{r} - \vec{R}_N) \times \vec{p}]}{||\vec{r} - \vec{R}_N||^3} \bullet \vec{\mu}_{nuc} \\ &+ \frac{1}{2c^2}\frac{[(\vec{r} - \vec{R}_N) \times \vec{\mu}_{nuc}]}{||\vec{r} - \vec{R}_N||^3} \bullet [(\vec{r} - \vec{R}_G) \times \vec{B}] \\ &+ \frac{1}{8c^2}||(\vec{r} - \vec{R}_G) \times \vec{B}||^2 \end{aligned} \tag{2.2}$$

If the nuclear contribution is neglected, the above simplifies to the following form.

$$\hat{H} = \hat{H}^0 + \frac{1}{2c}[(\vec{r} - \vec{R}_G) \times \vec{p}] \bullet \vec{B} + \frac{1}{8c^2}||(\vec{r} - \vec{R}_G) \times \vec{B}||^2 \tag{2.3}$$

In Eq.(2.3), the first term inside the curly bracket is $\vec{m} \bullet \vec{B}$, where $\vec{m}$ is the magnetic analogue of dipole moment known as magnetic moment [21]. The magnetic moment of the molecule is given as

$$\hat{m} = -\frac{1}{2}\sum_i [(\vec{r}_i - \vec{R}_G) \times \vec{p}_i] \tag{2.4}$$

In the above equation, the term in the square bracket on the right hand side is the orbital angular momentum operator. $\vec{R}_G$ is gauge origin. For open-shell systems, there is an additional term due to spin. For closed-shell systems, the magnetic moment is zero. The second term in Eq. (2.3) comes from the the diamagnetic contribution to the magnetizability of the molecule. The diamagnetic magnetizability operator [22] is given by

$$\hat{\chi}^{d}_{\alpha\beta} = -\frac{1}{4}\sum_{i}[(\vec{r}_i - \vec{R}_G)^2\delta_{\alpha\beta} - (\vec{r}_{i,\alpha} - \vec{R}_{G,\alpha})(\vec{r}_{i,\beta} - \vec{R}_{G,\beta})] \tag{2.5}$$

There is one more contribution to the magnetizability of the molecule from the orbital and spin angular momenta, commonly referred to as paramagnetic magnetizability. It is the magnetic analogue of dipole polarizability and is obtained as derivative of the magnetic moment of the molecule with respect to the external magnetic field. For closed shell molecule, the spin angular momentum being zero, the paramagnetic contribution to magnetizability comes through orbital angular momentum only.

The total magnetizability is the sum of the diamagnetic and paramagnetic contribution, and is the second order energy derivative with respect to uniform external magnetic field. While, the paramagnetic contribution is obtained using linear response of the energy anasatz, the diamagnetic contribution can simply be obtained as the expectation value of the operator given in Eq. (2.5)

## 2.3 Extended Coupled Cluster Method

ECC method uses a bi-orthogonal CC functional. The ECC approach was proposed by Arponen and co-workers [5, 27], in which, the energy of the system can be expressed in terms of double-similarity transformed Hamiltonian as opposed to the NCC method, where, a single similarity transformation is used. In the ECC method, the expectation value is constructed using bi-orthogonal right and left wave functions

$$E^0 =< \Psi'|\hat{H}|\Psi > \tag{2.6}$$

with

$$\begin{aligned} < \Psi'|\Psi > &= 1 \\ < \Phi_0|\Psi > &= 1 \end{aligned} \tag{2.7}$$

Using $|\Psi >$ as $\mathbf{e}^{\tau}\mathbf{e}^{-S}|\Phi_0 >$, where $\Phi_0$ is Hartree-Fock determinant, $\tau$ is hole-particle creation (excitation) operator with respect to $\Phi_0$ vacuum, $S$ is hole-particle destruction (de-excitation) operator and $< \Psi'|$ as $< \Phi_0|\mathbf{e}^{S}\mathbf{e}^{-\tau}$, one can construct $E_0$ as double-similarity transformed Hamiltonian.

$$E^0 =< \Phi_0|\mathbf{e}^{S}\mathbf{e}^{-\tau}\hat{H}\mathbf{e}^{\tau}\mathbf{e}^{-S}|\Phi_0 > \tag{2.8}$$

The hole-particle creation and destruction operators $\tau$ and $S$, respectively can be decomposed into different many-body components.

$$\begin{aligned} \tau &= \tau_1 + \tau_2 + \ldots + \tau_n \\ \tau_1 &= \sum_{i,\alpha} \tau_i^{\alpha}\{a_{\alpha}^{\dagger}a_i\} \\ \tau_2 &= \sum_{i,j,\alpha,\beta} \tau_{ij}^{\alpha\beta}\{a_{\beta}^{\dagger}a_{\alpha}^{\dagger}a_i a_j\}\text{and so on.} \end{aligned} \tag{2.9}$$

$$\begin{aligned} S &= S_1 + S_2 + \ldots + S_n \\ S_1 &= \sum_{i,\alpha} s_{\alpha}^{i}\{a_i^{\dagger}a_{\alpha}\} \\ S_2 &= \sum_{i,j,\alpha,\beta} s_{\alpha\beta}^{ij}\{a_i^{\dagger}a_j^{\dagger}a_{\beta}a_{\alpha}\}\text{and so on.} \end{aligned} \tag{2.10}$$

and so on. Eq.(2.8) may be simplified by transforming the set $\{\tau\}$ to another set $\{T\}$ of excitation operators as shown by Arponen [27]. The set of $T$-amplitudes are defined as,

$$T|\Phi_0 >= (1 - |\Phi_0 >< \Phi_0|)\mathbf{e}^{S}\tau|\Phi_0 > \tag{2.11}$$

In the above transformation, all the $S$-vertices, which are fully contracted to $\tau$ vertices, are all absorbed leading to a new set of hole-particle creation operators, the

$T$-operators. Like $\tau$, the $T$ operators can also be expanded in terms of creation and annihilation operators analogously. This eliminates any term in the energy functional, where $\{S\}$ can be exclusively connected to a single $\{T\}$-vertex. This leads to a double-linked form of energy functional.

$$E_0 =< \Phi_0|\mathbf{e}^S[H\mathbf{e}^T]_L|\Phi_0 >_{DL} \tag{2.12}$$

In the Eq. (2.12) the subscript $L$ indicates direct linking of the $T$-amplitudes to the Hamiltonian and the subscript $DL$ (double or defined linking) imposes further restriction on linking of $\{S\}$, i.e. the $S$-amplitudes should either be directly linked to the Hamiltonian, or to minimum two distinct $T$-amplitudes. The double-linking in Eq.(2.12) leads to connectedness in the terms for the energy expression as well as for the cluster equations assuring size-extensivity as verified by Piecuch and Bartlett [32].

The definition of $\{T\}$ incorporates in $T$, the perturbation corrections from the contractions of $S$ and $\tau$ up to infinite order. Thus, the double-linked energy anasatz is not only size-extensive, but also, perturbatively and more accurate and superior. The Eq.(2.12) also ensures natural termination of the series. However, the natural truncation occurs at quite high perturbation order, e.g., for singles and doubles approximation, the term with maximum number of $S$ and $T$ amplitudes is $S_1^6 V T_2^4$, i.e. total power $(S+T) = 10$ and the perturbation order of this term is 17. However, the terms of such a high perturbation order hardly affect the results. Moreover, the inclusion of terms up to total power $(S + T) = 10$ is computationally quite expensive. The series therefore needs to be artificially truncated for practical purpose. Head-Gordon *et. al.* [29] used Bruckner orbitals to eliminate singles and proposed quadratic truncation for left and right cluster amplitudes, which was found to give accurate results for energy for various systems. The amplitudes for $S$ and $T$ can be obtained variationally, i.e., by making the energy expression stationary with respect to the cluster amplitudes $t$ and $s$ respectively.

$$\begin{aligned}\frac{\partial E^{(0)}}{\partial t_i} &= 0; i = 1....n \\ \frac{\partial E^{(0)}}{\partial s_i} &= 0; i = 1....n \end{aligned} \tag{2.13}$$

The method, being variational both in $T$ as well as in $S$ is also referred to as bi-variational coupled cluster method. Because of the variational nature, the Hellmann-Feynman theorem holds, due to which, there is a (2n +1) rule for evaluating the energy response properties. Thus, the first order properties can be obtained by the knowledge the amplitudes of $T$ and $S$ only.

In order to evaluate the second and the third order response properties, one needs to know the first derivatives of $T$ and $S$amplitudes. These are obtained by differentiating the explicit expression for the first derivative of energy $E^{(1)}$, which can be written as

$$\begin{aligned}E^{(1)} &= <\Phi_0|\mathbf{e}^S[H^{(1)}\mathbf{e}^T]_L|\Phi_0>_{DL} \\ &\quad + <\Phi_0|\mathbf{e}^S\{S^{(1)}[H\mathbf{e}^T]_L + [H\mathbf{e}^T T^{(1)}]_L\}|\Phi_0>_{DL}\end{aligned} \tag{2.14}$$

where the subscripts $L$ and $DL$ are as defined in the Eq.(2.12). The double-linked structure of Eq.(2.14) leads to the connectivity of terms for the derivative cluster amplitudes obtained by imposing stationarity condition on $E^{(1)}$ with respect to amplitudes of $T^{(0)}$ and $S^{(0)}$ respectively.

$$\begin{aligned}\frac{\partial E^{(1)}}{\partial t_i} &= 0; i = 1....n \\ \frac{\partial E^{(1)}}{\partial s_i} &= 0; i = 1....n \end{aligned} \tag{2.15}$$

The Eqs.(2.15) provide us with the first derivative $T^{(1)}$ and $S^{(1)}$ operators and subsequently, properties up to third order can be obtained. The ECC response approach with singles and doubles approximation and with cubic total truncation of the cluster amplitudes in the energy expression (cubic-ECCSD) was used by Pal and co-workers [30, 31] and has been found to give fairly accurate results for electric properties. Pal and co-workers have used this method for evaluation of dipole moments, polarizabilities and first hyperpolarizabilities of various systems at equilibrium geometry. Behavior of the properties at single bond stretch has also been studied. However, as mentioned in the introduction, there have been no studies for magnetic properties of molecules using ECC response approach. The current chapter discusses about the performance of ECC method for magnetizabilities of some diatomic molecules.

## 2.4 Results and Discussion

We now present test results for diamagnetic and paramagnetic magnetizabilities of hydrogen fluoride and carbon monoxide at the equilibrium bond distance. The components of diamagnetic magnetizability in the directions parallel and perpendicular to the molecular axis have been reported. In case of paramagnetic magnetizability, the parallel components being identically zero for both these systems, have not been presented in the tables. We have computed the magnetizabilities of these molecules using moderately large Gaussian orbital basis sets as some reasonable gauges to study the gauge dependence of the magnetizabilities at ECC level. The required integrals were obtained from "DALTON, *a molecular electronic structure program Release* 1.2, (2001)" [33].

For HF, we have studied the magnetizabilities using four basis sets, *viz.* cc-pVDZ, cc-pVTZ and augmentation of these with diffuse functions. For CO, we have used cc-pVDZ and augmented cc-pVDZ basis sets. Due to computation expenses, the calculations with larger basis sets have not been done for this system. Since the magnetizabilities are gauge-dependent, proper gauge should be chosen for accurate results. The gauge origin at the maximum electron density is expected to give good results for magnetizabilities, which can be seen from the expressions for the operators defined earlier in this section. With this point of view, we have selected the gauge origins while studying these systems. For the magnetizabilities of hydrogen fluoride we have chosen the gauge origins at the F nucleus and centre of mass respectively. In case of carbon monoxide, the calculations have been done by choosing the gauge origin at centre of mass and at the mid-point of the C–O bond respectively for the magnetizability calculations, since the electron density is evenly spread between these nuclei.

Table 2.1: Magnetizabilities of Hydrogen Fluoride

| Basis set | Gauge origin | Method | $\chi_{\perp}^{d}$ | $\chi_{\parallel}^{d}$ | $\chi_{\perp}^{p}$ | $\chi_{total}$ |
|---|---|---|---|---|---|---|
| cc-pVDZ | F | RHF | -2.3094 | -2.0036 | 0.1746 | -2.0911 |
| | | ECC | -2.3433 | -2.0162 | 0.1911 | -2.1068 |
| | | NCC | -2.3433 | -2.0162 | | |
| | c.m. | RHF | -2.2863 | -2.0036 | 0.1535 | -2.0898 |
| | | ECC | -2.2989 | -2.0162 | 0.1705 | -2.0910 |
| | | NCC | -2.3182 | -2.0162 | | |
| aug-cc-pVDZ | F | RHF | -2.4114 | -2.1275 | 0.1636 | -2.2077 |
| | | ECC | -2.4860 | -2.1916 | 0.1783 | -2.2690 |
| | | NCC | -2.4879 | -2.1934 | | |
| | c.m. | RHF | -2.3880 | -2.1275 | 0.1385 | -2.2089 |
| | | ECC | -2.4604 | -2.1916 | 0.1542 | -2.2680 |
| | | NCC | -2.4623 | -2.1934 | | |
| cc-pVTZ | F | RHF | -2.3561 | -2.0616 | 0.1752 | -2.1412 |
| | | ECC | -2.3953 | -2.0845 | 0.1950 | -2.1617 |
| | | NCC | -2.3955 | -2.0846 | | |
| | c.m. | RHF | -2.3329 | -2.0616 | 0.1519 | -2.1412 |
| | | ECC | -2.3701 | -2.0845 | 0.1743 | -2.1587 |
| | | NCC | -2.3703 | -2.0846 | | |
| aug-cc-pVTZ | F | RHF | -2.4016 | -2.1177 | 0.1727 | -2.1919 |
| | | ECC | -2.4598 | -2.1678 | 0.1921 | -2.2344 |
| | | NCC | -2.4610 | -2.1693 | | |
| | c.m. | RHF | -2.3781 | -2.1177 | 0.1475 | -2.1930 |
| | | ECC | -2.4343 | -2.1678 | 0.1700 | -2.2322 |
| | | NCC | -2.4355 | -2.1693 | | |
| Experimental[a] | | | | | 0.1760 | |

[a] See [34].

All results are in atomic units.

Table 2.1 presents the magnetizabilities of Hydrogen Fluoride at equilibrium geometry. For comparison, the NCCSD [33] results for diamagnetic magnetizability have been presented. The experimental results [34] for the perpendicular component of paramagnetic magnetizability are also presented. We observe that the present ECCSD results are generally in agreement with the NCCSD results for diamagnetic magnetizability. For every gauge, the NCCSD values for $\chi_{\perp}^{d}$ and $\chi_{\parallel}^{d}$ are marginally lower than the corresponding ECCSD values.

For $\chi_{\perp}^{p}$, our results can only be compared against the experimental values, since NCCSD values for the same are not available. We also observe the basis set effects on these values. Generally, the effects of augmenting by diffuse functions lower, the diamagnetic magnetizability values systematically. Since these are negative, the absolute values increase. This effect is same for the NCCSD method. The effect of augmentation is marginally more for $\chi_{\perp}^{d}$. For the $\chi_{\parallel}^{p}$, however, we find that augmentation from cc-pVDZ to aug-cc-pVDZ reduces the values, but a similar augmentation of cc-pVTZ reduces the values only marginally. Similarly, we can observe the change in the basis from cc-pVDZ to extensive cc-pVDZ basis. We find the decrease in the $\chi_{\perp}^{d}$ and $\chi_{\parallel}^{d}$ values (increase in the absolute values) and increase in $\chi_{\parallel}^{p}$ values at every gauge. With a large change in the augmentation in cc-pVDZ, for diamagnetic magnetizability values, we observe that the values increase (absolute values decrease) as we go from aug-cc-pVDZ to aug-cc-pVTZ basis. With this change, the paramagnetic magnetizability value increases much more significantly, than due to the change in the basis from cc-pVDZ to cc-pVTZ. Finally, we observe that the gauge-dependence of these values is only marginal for $\chi^{d}$ with marginal increase of $\chi_{\perp}^{d}$ values as the gauge origin is changed from the F nucleus to the centre of mass. The $\chi_{\perp}^{p}$ values decrease with the change in gauge origin from fluorine atom to the centre of mass. However, the results clearly show that both these gauges provide results within acceptable accuracy.

Table 2.2 presents results of magnetizabilities of Carbon monoxide at equilibrium distance. The experimental [35] and NCCSD results are also presented.

Table 2.2: Magnetizabilities of Carbon monoxide

| Basis set | Gauge origin | Method | $\chi^d_\perp$ | $\chi^d_\parallel$ | $\chi^p_\perp$ | $\chi_{total}$ |
|---|---|---|---|---|---|---|
| cc-pVDZ | c.m. | RHF | -8.0149 | -3.7286 | 4.8126 | -3.3778 |
|  |  | ECC | -8.0172 | -3.7421 | 3.0988 | -4.5771 |
|  |  | NCC | -8.0182 | -3.7421 |  |  |
|  | c.bond. | RHF | -8.1031 | -3.7286 | 4.8363 | -3.4207 |
|  |  | ECC | -8.0935 | -3.7421 | 3.2756 | -4.4593 |
|  |  | NCC | -8.0942 | -3.7421 |  |  |
| aug-cc-pVDZ | c.m. | RHF | -8.1014 | -3.8098 | 4.9862 | -3.3468 |
|  |  | ECC | -8.1401 | -3.8616 | 3.2344 | -4.5758 |
|  |  | NCC | -8.1417 | -3.8619 |  |  |
|  | c.bond. | RHF | -8.1904 | -3.8098 | 5.0738 | -3.3477 |
|  |  | ECC | -8.2187 | -3.8616 | 3.4428 | -4.4711 |
|  |  | NCC | -8.2200 | -3.8619 |  |  |
| Experimental[a] |  |  |  |  | 5.8738 |  |

[a] See [35].

All results are in atomic units.

There is a general agreement of the ECCSD results with NCCSD ones. Both components of diamagnetic magnetizability increase only marginally in ECCSD compared to NCCSD results. The gauge-dependence of $\chi^d$ is also not very significant. We also study the effect of augmentation in the basis. The results of $\chi^d$ decrease with addition of diffuse functions. For $\chi^p_\perp$ we do not have comparative NCCSD results. The values of $\chi^p_\perp$ increase with the addition of diffuse functions. The gauge-dependence is marginal. The CO, however represents a more difficult case as seen from the experimental value of $\chi^p_\perp$.

## 2.5 Conclusion

From the results presented in this chapter, it can be concluded that the magnetizabilities can be efficiently obtained from ECC response method under singles and doubles approximation. The preliminary implementation of ECC for magnetizabilities of hydrogen fluoride and carbon monoxide for different choice of gauge origins have been presented and compared with uncorrelated as well as correlated methods and some experimental results. It is seen that with proper choice of gauge origins, the variation of results with gauge is only marginal. The correlation effects in case of CO are quite prominent from the fact that the paramagnetic magnetizability is still quite different from the experimental result. Further accuracy may however, be achieved only after incorporation of one of the techniques used for gauge-invariance in the ECC framework.

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# *Chapter 3*

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# Constrained variational response to FSMRCC one valence problems: First order properties

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## 3.1 Introduction

Recently, MRCC methods [1–8] have emerged as methods of choice for accurate description of the behavior of quasi-degenerate molecular systems. Various subclasses of MRCC have come up depending on the way they handle the non-dynamical and dynamical electron correlation effects. Amongst them, the methods which formulate effective Hamiltonian provide multiple roots via diagonalization of the effective Hamiltonian within the model space and have been well studied. Mainly two approaches belong to this subclass, namely, FSMRCC [1–3, 7] and HSMRCC [4, 5]. Both these approaches differ in their windows of applicability due to the merits and demerits, inherent in their formulations. The potential energy surfaces (PES), for example, can be better studied using HSMRCC. FSMRCC, on the other hand, describes well, the cases like ionization, electron-attachment and electronically excited states of molecules, i.e. the cases, we are interested in. Alternately, some SR based methods like SAC-CI [9–11], EOM-CC [12–14] have also been successful in handling certain kinds of quasi-degeneracies.

As discussed in Chapter 1, FSMRCC assumes a common vacuum. Usually, the ground state RHF of the nearest closed-shell is chosen as vacuum. The model space configurations are formed by addition and/or removal of electrons to/from a set of orbitals termed as active orbitals. The model space configurations and the corresponding FS sector is represented in terms of the particle-occupancy of the configurations with respect to the vacuum. For, if $N$-electron RHF is vacuum, the model space of $(N-1)$-electron will be represented by $(0,1)$ sector of FS, $(N+1)$-electron model space by $(1,0)$ FS sector and $N$-electron excited states by $(1,1)$ sector of FS and so on, the vacuum being $(0,0)$ sector of FS. The ionized and electron-attached states belong to one-valence FS problem, since, they have single occupancy in model space in terms of hole-particles. Analogously, the excited states belong to two-valence problem in FSMRCC context.

To increase scope of applicability of a method for general electronic structure calculations, it is important to formulate its linear response. In FSMRCC context, this development was started by Pal [15] and was similar to Monkhorst's approach in SRCC methods [16]. The method was later implemented by Pal and co-workers [17, 18], Hirao and co-workers [19] and Ajitha *et. al.* [20] for analytical dipole moments of various open-shell molecular systems and excited states. However, this was quite unsatisfactory as the energy derivatives required time consuming evaluations of cluster amplitude derivatives up to that order, separately, for every mode of perturbation. A more concrete formulation along the lines of SRCC analytical response could be obtained only using CVA. Szalay [21] formulated CVA-FSRMCC and used for gradients. However, the method was applicable for CMS only. Formulation of CVA-FSMRCC for general IMS was developed by Shamasundar *et. al.* [22], which simplifies to the Szalay's formulation in case of CMS. We have done the computational developments of CVA-FSMRCC formulated by Shamasundar *et. al.* with SD approximation (CVA-FSMRCCSD) for ionized, electron-attached and excited states. In our present developments, we have neglected the effect of relaxation of orbitals due to external perturbation. In this chapter, we present the first part of our development, i.e. implementation of CVA-FSMRCC for the first order energy derivatives of ionized and electron-attached states. This is a step towards the CVA-FSMRCC formulation for excited states. Ionization or electron-addition to closed-shell molecules results in open-shell doublet molecules, commonly known as radicals. Understanding the importance of free radicals [23] in various fields like atmospheric chemistry, biochemistry and plasma chemistry, we present in this chapter, dipole moments of some small free radicals as test examples.

## 3.2 CVA-FSMRCC method for the first order properties

The FSMRCC theory has already been described in Chapter 1 for a general $(p, h)$-valence sector. Here, we rewrite the algebra specifically for $(0, 1)$-sector of FS to discuss the formulation of CVA in FSMRCC context. The configurations of this CMS are given by

$$|\Psi_{\mu}^{(0,1)} >= \sum_{i} C_{i\mu} |\Phi_{i}^{(0,1)} > \tag{3.1}$$

The dynamical electron correlation effects are brought in through a universal wave operator $\Omega$.

$$\Omega = \{e^{\tilde{T}^{(0,1)}}\} \tag{3.2}$$

$$\tilde{T}^{(0,1)} = T^{(0,1)} + T^{(0,0)} \tag{3.3}$$

The wave operator $\Omega$ is parameterized such that the states generated by its action on the reference function satisfy Bloch-Lindgren equation for effective Hamiltonian given by Eq. (1.65). The lower valence cluster operator equations are decoupled from the higher valence ones, commonly known as subsystem embedding condition (SEC). 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.

$$H_{\mathit{eff}}^{(0,1)}C^{(0,1)} = C^{(0,1)}E$$
$$\tilde{C}^{(0,1)}H_{\mathit{eff}}^{(0,1)} = E\tilde{C}^{(0,1)} \tag{3.4}$$

Explicit differentiation of the above equations leads to the non-variational LR of FSMRCC and involves solution of derivatives of $\Omega$ and $H_{\mathit{eff}}^{(0,1)}$ for every mode of perturbation separately.

We now briefly discuss the CVA-FSMRCC method for $(0,1)$ Fock space. The energy of a specific state of the ionized system is given by

$$E_\mu = \sum_{ij} \tilde{C}_{\mu i}^{(0,1)}(H_{\mathit{eff}})_{ij}^{(0,1)}C_{j\mu}^{(0,1)} \tag{3.5}$$

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

$$\begin{aligned}
\Im \; = \; & \sum_{ij} \tilde{C}_{\mu i}^{(0,1)}(H_{\mathit{eff}})_{ij}^{(0,1)}C_{j\mu}^{(0,1)} \\
& + P^{(0,1)}\Lambda^{(0,1)}P^{(0,1)}P^{(0,1)}[H\Omega - \Omega H_{\mathit{eff}}^{(0,1)}]P^{(0,1)} \\
& + P^{(0,1)}\Lambda^{(0,1)}Q^{(0,1)}Q^{(0,1)}[H\Omega - \Omega H_{\mathit{eff}}^{(0,1)}]P^{(0,1)} \\
& + P^{(0,0)}\Lambda^{(0,0)}P^{(0,0)}P^{(0,0)}H\Omega P^{(0,0)} \\
& + P^{(0,0)}\Lambda^{(0,0)}Q^{(0,0)}Q^{(0,0)}H\Omega P^{(0,0)} \\
& - E_\mu\left(\sum_{ij}\tilde{C}_{\mu i}^{(0,1)}C_{j\mu}^{(0,1)} - 1\right)
\end{aligned} \tag{3.6}$$

The $\Lambda$ in Eq. (3.6) 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 multipliers vanishes. The Eq. (3.6) thus reduces to

$$\begin{aligned}\Im &= \sum_{ij} \tilde{C}^{(0,1)}_{\mu i} (H_{\textit{eff}})^{(0,1)}_{ij} C^{(0,1)}_{j\mu} \\ &+P^{(0,1)}\Lambda^{(0,1)}Q^{(0,1)}Q^{(0,1)}[H\Omega - \Omega H^{(0,1)}_{\textit{eff}}]P^{(0,1)} \\ &+P^{(0,0)}\Lambda^{(0,0)}Q^{(0,0)}Q^{(0,0)}H\Omega P^{(0,0)} \\ &-E_\mu \left( \sum_{ij} \tilde{C}^{(0,1)}_{\mu i} C^{(0,1)}_{j\mu} - 1 \right) \qquad (3.7)\end{aligned}$$

Differentiation of Eq. (3.7) with respect to $\Lambda$ results in expression for cluster amplitudes, i.e., the Bloch equation. It is obviously seen that the equations for $\Omega$ amplitudes are decoupled from the $\Lambda$ amplitudes. The $\Lambda$ equations are, however, coupled with the $\Omega$ amplitudes. These are obtained by making Eq. (3.7) stationary with respect to the cluster amplitudes. In presence of external field, the Lagrangian and the parameters $\Upsilon \ = \{H_{\textit{eff}}, C, \tilde{C}, E, \Omega, \Lambda\}$ become perturbation dependent. These can be expanded in Taylor series.

$$\Upsilon(g) = \Upsilon^{(0)} + g\Upsilon^{(1)} + \frac{1}{2!}g^2\Upsilon^{(2)} + \frac{1}{3!}g^3\Upsilon^{(3)} + \dots \qquad (3.8)$$

The Lagrangian defined in Eq. (3.7) 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

$$\begin{aligned}\Im^{(0)} &= \left( \tilde{C}^{(0,1)(0)} H^{(0,1)(0)}_{\textit{eff}} C^{(0,1)(0)} \right)_{\mu\mu} \\ &+P^{(0,1)}\Lambda^{(0,1)(0)}[H^{(0)}\Omega^{(0)} - \Omega^{(0)} H^{(0,1)(0)}_{\textit{eff}}]P^{(0,1)} \\ &+P^{(0,0)}\Lambda^{(0,0)(0)}[H^{(0)}\Omega^{(0)}]P^{(0,0)} \\ &-E_\mu \left( \sum_{ij} \tilde{C}^{(0,1)(0)}_{\mu i} C^{(0,1)(0)}_{j\mu} - 1 \right) \qquad (3.9)\end{aligned}$$

$$
\begin{aligned}
\Im^{(1)} \;=\;& \left(\tilde{C}^{(0,1)(1)} H_{\mathit{eff}}^{(0,1)(0)} C^{(0,1)(0)}\right)_{\mu\mu} + \left(\tilde{C}^{(0,1)(0)} H_{\mathit{eff}}^{(0,1)(1)} C^{(0,1)(0)}\right)_{\mu\mu} \\
& + \left(\tilde{C}^{(0,1)(0)} H_{\mathit{eff}}^{(0,1)^{(0)}} C^{(0,1)^{(1)}}\right)_{\mu\mu} \\
& + P^{(0,1)}\Lambda^{(0,1)(1)}[H^{(0)}\Omega^{(0)} - \Omega^{(0)} H_{\mathit{eff}}^{(0,1)(0)}]P^{(0,1)} \\
& + P^{(0,1)}\Lambda^{(0,1)(0)}[H^{(1)}\Omega^{(0)} + H^{(0)}\Omega^{(1)} - \Omega^{(1)} H_{\mathit{eff}}^{(0,1)(0)} - \Omega^{(0)} H_{\mathit{eff}}^{(0,1)(1)}]P^{(0,1)} \\
& + P^{(0,0)}\Lambda^{(0,0)(1)} H^{(0)}\Omega^{(0)} P^{(0,0)} + P^{(0,0)}\Lambda^{(0,0)(0)} H^{(1)}\Omega^{(0)} + H^{(0)}\Omega^{(1)} P^{(0,0)} \\
& - E_{\mu}^{(0)} \sum_{ij} \left(\tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(1)} + \tilde{C}_{\mu i}^{(0,1)(1)} C_{j\mu}^{(0,1)(0)}\right) \\
& - E_{\mu}^{(1)} \left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(0)} - 1\right)
\end{aligned}
\tag{3.10}
$$

The Eqs. (3.9) and (3.10) give the energy and the first order energy derivative for the state $\mu$. Because of stationarity of Lagrangian with respect to $\Lambda$ and $\Omega$, the above expressions are further simplified. The energy derivatives follow $(2n+1)$ rule with respect to the $\Omega$ amplitudes and $(2n+2)$ rule with respect to $\Lambda$ 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. (3.9) and (3.10) simplify. We denote this simplified Lagrangian as $\Im_{\mathit{opt}}$.

$$
\Im_{\mathit{opt}}^{(0)} = \left(\tilde{C}^{(0,1)(0)} H_{\mathit{eff}}^{(0,1)(0)} C^{(0,1)(0)}\right)_{\mu\mu}
\tag{3.11}
$$

$$
\begin{aligned}
\Im_{\mathit{opt}}^{(1)} \;=\;& \left(\tilde{C}^{(0,1)(0)} H_{\mathit{eff}\Omega^{(0)}}^{(0,1)(1)} C^{(0,1)(0)}\right)_{\mu\mu} \\
& + P^{(0,1)}\Lambda^{(0,1)(0)}[H^{(1)}\Omega^{(0)} - \Omega^{(0)} H_{\mathit{eff}\Omega^{(0)}}^{(0,1)(1)}]P^{(0,1)} \\
& + P^{(0,0)}\Lambda^{(0,0)(0)} H^{(1)}\Omega^{(0)} P^{(0,0)}
\end{aligned}
\tag{3.12}
$$

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 $\Omega$ and $\Lambda$ amplitudes only. Differentiation of Eq. (3.9) with respect to $\Lambda$ amplitudes leads the equations for $\Omega$ amplitudes – the Bloch equations. The $\Lambda$ are obtained by differentiating Eq. (3.9) with respect to $\Omega$ amplitudes. It may be noticed that the coupling within the $\Lambda$ amplitudes in various valence sectors is exactly opposite of SEC. Thus, one has to solve for the $\Lambda$ amplitudes successively from the highest valence sector to the lowest valence sector.

The CVA method is a single-root method. The $\Lambda$ amplitudes depend on the desired state of the molecule. Therefore, for every state one has to calculate the $\Lambda$ amplitudes separately. In contrast, the non-variational response of FSMRCC [15] 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 $\Lambda$ equations for one-valence problem are same as the "zeta equations" in the EOMCC method [14, 24].

## 3.3 Computational details

The universal wave operator $\Omega$ in case of the ionized states is $[e^{T^{(0,0)}}e^{T^{(0,1)}}]$, whereas for the electron attached radicals, it is $[e^{T^{(0,0)}}e^{T^{(1,0)}}]$. In both the cases, the $T^{(0,0)}$ equations are decoupled from the valence sector $T$ equations due to SEC. Hence, we first solve for the $(0,0)$ sector amplitudes. These amplitudes once obtained, remain unchanged throughout the further calculations. Hence, for computational convenience, we store the $[\hat{H}e^{(T^{(0,0)}}]_C$ intermediates, 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 up to three body parts contribute to the valence sector cluster equations as well as to the $\Lambda$ 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 in the beginning of valence sector calculation and are stored in RAM or hard-disk depending on the size.

The equations for $\Lambda$ amplitudes are inhomogeneous linear simultaneous equations and as explained earlier, the $\Lambda$ amplitudes of the valence sector are first obtained; followed by solution of the $\Lambda$ amplitudes of the $(0,0)$ sector. The Jacobi's iterative procedure has been used for obtaining the $\Lambda$ amplitudes.

## 3.4 Results and Discussion

We, now, present the dipole moment results for OH, OOH and HCOO radicals, CH and SiH radicals and NO and $NO_2$ using CVA-FSMRCC. We have compared the results with the available benchmark results. As mentioned earlier, in our analytical results, the orbital relaxation effects have been neglected. The deviation of the CVA-FSMRCCSD results from the ones obtained using finite field (FF) methods is indeed due to this approximation. For the finite field FSMRCCSD results the energy calculations have been done with external electric field $0.000$ and $\pm 0.001$ atomic units respectively.

### 3.4.1 Ionized states

Some radicals can represented by ionized states of corresponding anions. We discuss the results of some of these radicals here. If the RHF of the closed shell anion is considered as vacuum, the model space configuration of the radicals belongs to $(0,1)$-sector of the FS. In particular, we present the dipole moment results for hydroxy, hydroperoxy and formyloxyl radicals. The geometries used been used for all the calculations and are provided in the Appendix. The SCF calculations were done using HONDO.

### *Hydroxy radical*

Table 3.1 gives the dipole moments for the $^2\Pi$ states of hydroxy radical. The cc-pVDZ basis set [25] has been used. The RHF of hydroxide anion is the choice of vacuum. The HOMO has two-fold degeneracy. Removal of an electron from one of these HOMOs leads to degenerate doublet ($^2\Pi$) state of hydroxy radical. We also report the results obtained using unrelaxed EOMCC [26] and Full Configuration Interaction (FCI) [27] method. It is seen that results are in good agreement with unrelaxed EOMCC method.

Table 3.1: Dipole moment of hydroxy radical

| CVA-FSMRCCSD | EOMCC(Unrelaxed)[a] | FCI[b] |
|---|---|---|
| 0.634 | 0.639 | 0.663 |

[a] See Ref. [26]

[b] See Kállay *et. al.* [27].

All results are in atomic units.

### *Hydroperoxy radical*

Dipole moment calculations for hydroperoxy radical were done using the double zeta basis set of Huzinaga Dunning [28] with a set of uncontracted polarized functions. We start with the RHF of hydroperoxide anion as vacuum. The electronic configuration of RHF of hydroperoxide anion is

$$[core], 3a_1^2, 4a_1^2, 5a_1^2, 1a_2^2, 6a_1^2, 7a_1^2, 2a_2^2$$

Removal of an electron from one of the last two occupied orbitals results in near-degenerate states ($^2A_2$ and $^2A_1$) of hydroperoxy radicals. The dipole moments of the radical along two orthogonal directions (y and x) have been presented in Table 3.2.

Table 3.2: Dipole moment of hydroperoxy radical

| Direction | State | CVA-FSMRCCSD | FF-FSMRCCSD |
|---|---|---|---|
| Y | ${}^2A_1$ | -0.676 | -0.700 |
|  | ${}^2A_2$ | -0.669 | -0.699 |
| X | ${}^2A_1$ | -0.367 | -0.418 |
|  | ${}^2A_2$ | -0.557 | -0.597 |

All results are in atomic units.

We also report the FF-FSMRCCSD calculations for the system. The orbital relaxation is seen to increase the magnitude of dipole moment slightly as seen from the analytical and FF results. Along both the orthogonal directions, the difference between the dipole moments of the reported states is, however, underestimated by FF method when compared with the corresponding results obtained by CVA-FSMRCCSD.

### ***Formyloxyl radical***

Table 3.3 gives the dipole moments for the first two low-lying near-degenerate states of formyloxyl radical.

Table 3.3: Dipole moment of formyloxyl radical

| State | CVA-FSMRCCSD | EOMCC[a] | FF-FSMRCCSD |
|---|---|---|---|
| ${}^2B_2$ | 0.910 | 1.004 | 1.000 |
| ${}^2A_1$ | 0.786 |  | 0.865 |

[a] See Stanton and Gauss [24].
All results are in atomic units.

We start with the RHF of formate anion as vacuum. Double zeta basis set of Huzinaga Dunning [28] with a set of uncontracted polarized functions was used for the calculations. Removal of an electron from the formate anion results in formyloxyl radical, the near-degenerate low-lying states of which, have the electronic configurations

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

$$\text{and} \qquad [core], 3a_1^2, 2b_2^2, 4a_1^2, 5a_1^2, 3b_2^2, 1b_1^2, 1a_2^2, 6a_1^1, 4b_2^2$$

The dipole moments along the H-C bond axis for these states, denoted by $^2B_2$ and $^2A_1$ have been reported. The EOMCC result [24] for the ground state has also been reported. We also present the FF-FSMRCCSD results for both the states. As in case of hydroperoxy radicals, the orbital relaxation is seen to increase the dipole moment values for both the states. The difference in the dipole moments of the two states is, however, almost same in FF as well as analytical methods. radical, orbital relaxation effects are found to be very important in this case also, which is evident from the difference between the ground state dipole moment values obtained from CVA-FSMRCCSD and EOMCC respectively.

### 3.4.2 Electron-attached states

We now consider some radicals which can be represented as electron attached states of corresponding cations. The model space configurations of a radical belonging to this class corresponds to $(1, 0)$-sector of the FS with the RHF configurations of the corresponding cation as vacuum. We present the dipole moments for monoradicals of carbon and silicon (CH and SiH) and some oxides of nitrogen (NO and $NO_2$).

#### ***Carbon monohydride and Silicon monohydride radicals***

Table 3.4 gives the dipole moments for CH and SiH radicals. Sadlej basis set optimized for properties [30] has been used for these molecules with [5S 3P 2D] functions on carbon, [7S 5P 2D] functions on silicon and [3S 2P] functions on hydrogen.

Table 3.4: Dipole moments of carbon and silicon monohydrides

| Molecule | CVA-FSMRCCSD | FF-FSMRCC | UGA-CCSD[a] | Expt.[b] |
|---|---|---|---|---|
| CH | 0.543 | 0.520 | 0.535 | 0.574<br>±0.023 |
| SiH | 0.063 | 0.046 | 0.037 | |

[a] See [29].

[b] Quoted in [31].

All results are in atomic units.

Both these radicals can be represented as electron attached states of the corresponding cations, namely CH$^+$ and SiH$^+$ respectively. The RHF configuration of these cations are chosen as vacua for the corresponding radicals. The two fold degenerate $\pi$ LUMOs are chosen to be active in case of CH$^+$ and SiH$^+$. The equilibrium geometries have been used for both these systems. For CH radical, the equilibrium bond distance between carbon and hydrogen is $2.11648a_0$ whereas, the equilibrium bond distance between silicon and hydrogen in SiH radical is $2.84a_0$. The dipole moments along the directions of internuclear axes have been reported. We compare our results with FF-FSMRCCSD response and UGA-CCSD [31]. We also present the experimental results [31] for CH radical. Our method is seen to produce result closer to the experimental result in case of CH radical. In case of SiH, the orbital relaxation seems to be very crucial as seen from large deviation of CVA-FSMRCCSD results from the other two methods.

### *Nitric oxide and nitrogen dioxide*

Table 3.5 gives the dipole moments for NO and NO$_2$ radicals. Sadlej basis set [30] has been used for these molecules with [5S 3P 2D] functions on nitrogen as well as on oxygen. These oxides of nitrogen can also be represented as electron attached states of the corresponding cations, namely NO$^+$ and NO$_2^+$ respectively. The RHF configuration of these cations are chosen as vacua for the corresponding radicals.

Table 3.5: Dipole moments of oxides of nitrogen

| Molecule | State | CVA-FSMRCCSD | FF-FSMRCCSD |
|---|---|---|---|
| NO | ($^2\Pi$) | -0.073 | -0.041 |
| | ($^2\Sigma$) | 0.674 | 0.698 |
| $NO_2$ | ($^2A_1$) | 0.141 | 0.176 |

All results are in atomic units.

For $NO^+$, the $\sigma$ orbital in the virtual space is also comparable in energy with the doubly degenerate $\pi$ LUMOs. We therefore choose these three orbitals of $NO^+$ as active orbitals. Addition of electron in one of the active orbitals results in the formation of the corresponding radicals. For both these states, we have reported the dipole moment along the direction of internuclear axis. We have used the ground state geometry of the molecule with the internuclear distance between nitrogen and oxygen $2.17464a_0$. The dipole moment is seen to change the direction as one goes from the ground state $^2\Pi$ to $^2\Sigma$ state. However, the effect of orbital relaxation is unidirectional in both the states due to which, the dipole moment results from the two methods differ significantly as compared to the excited state results.

For $NO_2$, we have used the ground state geometry as quoted by Hayes [32]. We start with the RHF of $NO_2^+$ as vacuum. $NO_2^+$ has LUMO with $A_1$ symmetry. Addition of a electron in this orbital gives the ground state of nitrogen dioxide radical which is the doublet $A_1$ state. We compare our analytical result with FF-FSMRCCSD results. In this case also, orbital relaxation is observed to increase the dipole moment value.

## 3.5 Conclusion

In this chapter, we have presented an implementation of CVA-FSMRCCSD method by taking the examples of open-shell radicals, which can be described by $(0, 1)$

and $(1, 0)$ Fock-space sectors. The method involves two sets of amplitudes, one normal Fock-space amplitudes and the other amplitudes of $\Lambda$-operator, having a structure conjugate to the Fock-space cluster operators. We observe that the method provides an efficient tool to obtain the first order properties without the cumbersome solution of the derivative cluster amplitudes. The orbital relaxation, however, seems to be important from the fact, that the analytical dipole moment results for all the systems studied in this chapter are found to differ significantly from the corresponding FF results.

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## *Chapter 4*

# Constrained variational response to FSMRCC one valence problems: Second order properties

### 4.1 Introduction

In the previous chapter, we discussed the CVA-FSMRCC formulation for obtaining first order energy derivatives for one-valence problems. The efficiency of the method is obtaining first order energy derivatives without the cumbersome evaluation of the first order derivatives of the cluster amplitudes was verified from the dipole moment results of various doublet radicals presented in the chapter. In continuation with the above mentioned work, we present in this chapter, extension of the one-valence CVA-FSMRCC anasatz for obtaining second order analytical energy derivatives. Recently, there also have been developments in other CC based formulations [1, 2] for obtaining higher order properties.

Although, the formulation of CVA-FSMRCC was presented earlier by Pal and co-workers [3], it took long time since then, for the computational developments. In FSMRCC framework, no computational developments in higher order analytical energy derivatives have been reported. In this chapter, we present the first applications in second order analytical properties using constrained variational response of FSMRCCSD anasatz. We have organized the chapter as follows. We first present the algebra for obtaining Lagrangian for second order energy derivatives in the next section. The simplifications in the Lagrangian by application of $(2n+1)$ and $(2n+2)$ rules [4, 5] will also be presented. We present analytical results for static polarizabilities of some doublet radicals as pilot applications of our computational developments.

## 4.2 CVA-FSMRCC method for the second order properties

In continuation with the theory discussed in Chapter 3, we now proceed for obtaining the Lagrangian for the second order energy derivatives. We write the algebra for $(0,1)$ sector of FS. The expressions for $(1,0)$ sector can be trivially obtained by interchanging the indices of holes and particles.

We start with the Lagrangian $\Im$ defined in Eq. (3.7). As mentioned in the previous chapter, the quantities $\Upsilon = \{H_{\textit{eff}}, C, \tilde{C}, E, \Omega, \Lambda\}$ become perturbation dependent along with $\Im$ and may be expressed as Taylor series of the external field $g$. Differentiating Eq. (3.7) twice with respect to $g$, we obtain the Lagrangian for second order energy derivative for specific root of the effective Hamiltonian.

$$
\begin{aligned}
\Im^{(2)} \;=\;& \left(\tilde{C}^{(0,1)(2)} H_{\textit{eff}}^{(0,1)(0)} C^{(0,1)(0)}\right)_{\mu\mu} + \left(\tilde{C}^{(0,1)(1)} H_{\textit{eff}}^{(0,1)(1)} C^{(0,1)(0)}\right)_{\mu\mu} \\
& +2\left(\tilde{C}^{(0,1)(1)} H_{\textit{eff}}^{(0,1)(0)} C^{(0,1)(1)}\right)_{\mu\mu} + \left(\tilde{C}^{(0,1)(0)} H_{\textit{eff}}^{(0,1)(2)} C^{(0,1)(0)}\right)_{\mu\mu} \\
& + \left(\tilde{C}^{(0,1)(0)} H_{\textit{eff}}^{(0,1)(1)} C^{(0,1)(1)}\right)_{\mu\mu} + \left(\tilde{C}^{(0,1)(0)} H_{\textit{eff}}^{(0,1)^{(0)}} C^{(0,1)^{(2)}}\right)_{\mu\mu} \\
& +P^{(0,1)}\Lambda^{(0,1)(2)}[H^{(0)}\Omega^{(0)} - \Omega^{(0)} H_{\textit{eff}}^{(0,1)(0)}]P^{(0,1)} \\
& +P^{(0,1)}\Lambda^{(0,1)(1)}[H^{(1)}\Omega^{(0)} + H^{(0)}\Omega^{(1)} - \Omega^{(0)} H_{\textit{eff}}^{(0,1)(1)} - \Omega^{(1)} H_{\textit{eff}}^{(0,1)(0)}]P^{(0,1)} \\
& +P^{(0,1)}\Lambda^{(0,1)(0)}[H^{(2)}\Omega^{(0)} + H^{(1)}\Omega^{(1)} + H^{(0)}\Omega^{(2)}]P^{(0,1)} \\
& -P^{(0,1)}\Lambda^{(0,1)(0)}[\Omega^{(0)} H_{\textit{eff}}^{(0,1)(2)} + \Omega^{(1)} H_{\textit{eff}}^{(0,1)(1)} + \Omega^{(2)} H_{\textit{eff}}^{(0,1)(0)}]P^{(0,1)} \\
& +P^{(0,0)}\Lambda^{(0,0)(2)}[H^{(0)}\Omega^{(0)}]P^{(0,0)} + P^{(0,0)}\Lambda^{(0,0)(1)}[H^{(1)}\Omega^{(0)} + H^{(0)}\Omega^{(1)}]P^{(0,0)} \\
& +P^{(0,0)}\Lambda^{(0,0)(0)}[H^{(2)}\Omega^{(0)} + H^{(1)}\Omega^{(1)} + H^{(0)}\Omega^{(2)}]P^{(0,0)} \\
& -E_{\mu}^{(0)} \sum_{ij} \left(\tilde{C}_{\mu i}^{(0,1)(2)} C_{j\mu}^{(0,1)(0)} + 2\tilde{C}_{\mu i}^{(0,1)(1)} C_{j\mu}^{(0,1)(1)} + \tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(2)}\right) \\
& -E_{\mu}^{(1)} \sum_{ij} \left(\tilde{C}_{\mu i}^{(0,1)(1)} C_{j\mu}^{(0,1)(0)} + \tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(1)}\right) \\
& -E_{\mu}^{(2)} \sum_{ij} \left(\tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(0)} - 1\right) \qquad (4.1)
\end{aligned}
$$

Following Shamasundar *et. al.* [3], some terms in Eq. (4.1) mutually cancel whereas several others vanish because of $(2n+1)$ and $(2n+2)$ rules [4]. If there is no operator form for $H^2$, the Eq. (4.1) simplifies after above cancellations to

$$
\begin{aligned}
\Im_{\textit{opt}}^{(2)} \;=\;& \left(\tilde{C}^{(0,1)(0)} H_{\textit{eff}}^{(0,1)(2)}{}_{\Omega^{(1)}} C^{(0,1)(0)}\right)_{\mu\mu} \\
& +P^{(0,1)}\Lambda^{(0,1)(0)}[H^{(2)}\Omega^{(0)} + H^{(1)}\Omega^{(1)} - (\Omega^{(0)} H_{\textit{eff}}^{(0,1)})_{\Omega^{(1)}}^{(2)}]P^{(0,1)} \\
& +P^{(0,0)}\Lambda^{(0,0)(0)}[H^{(1)}\Omega^{(1)} + H^{(0)}\Omega_{\Omega^{(1)}}^{(2)}]P^{(0,0)} \\
& +2\left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)(1)} H_{\textit{eff}}^{(0,1)(0)} C_{j\mu}^{(0,1)(1)} - E_{\mu}^{(0)} \sum_{i} \tilde{C}_{\mu i}^{(0,1)(1)} C_{i\mu}^{(0,1)(1)}\right) \qquad (4.2)
\end{aligned}
$$

‘ The subscripts $\Omega^{(0)}$ and $\Omega^{(1)}$ indicate that, the the corresponding terms are formed using up to zeroth and first derivatives of the cluster amplitudes respectively.

The second order properties can thus 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 $\Lambda$-vectors.

Due to single-root nature of the CVA method, one has to obtain the $\Lambda$ amplitudes separately for every state unlike the non-variational response of FSMRCC [6], which has has a multiple-root structure. However, the expensive evaluation of wave-function derivatives for each mode of perturbation is avoided in CVA-FSMRCC. This feature becomes more prominent while obtaining higher order properties like polarizability. 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. may be noted that for one-valence problem, FSMRCC method is equivalent to EOM-CC[7, 8]. However, developments in higher order linear response of EOM-CC have yet not been reported.

The computational strategies used for obtaining first order energy derivatives are transparently extended in case of second order derivatives. An additional step of evaluation of $T^{(0,0)}$ derivative amplitudes and storage of the resulting intermediates with Hamiltonian gets introduced this case.

## 4.3 Results and Discussion

In this section, we present static polarizabilities OH, OOH and HCOO radicals, obtained analytically using CVA-FSMRCCSD. We also present analytical results for static polarizabilities of of CH, SiH and NO radicals using CVA-FSMRCCSD. We compare the results with ones obtained using different theoretical methods and experimental results. Wherever finite field FSMRCC (both energy based and dipole based) results are reported, we have done the calculations using external electric field 0.000 and $\pm 0.001$ atomic units in the direction mentioned.

### 4.3.1 Ionized states

The OH, HCOO and OOH radicals can be represented as ionized states of the corresponding anions. We have used cc-pVDZ basis set [9] for OH radical. For HCOO and OOH radicals we have used Huzinaga-Dunning double zeta basis set augmented with a set of polarized functions. The exponents for these uncontracted polarized functions are 0.686 for hydrogen (P), 0.654 for carbon (D) and 1.211 for oxygen (D). The geometries for these molecules are mentioned in the Appendix. The polarizability components of OH, HCOO and OOH are given in Table 4.1. For polarizabilities, no results are available for these systems. Hence, we compare our results with energy based and dipole based FF results using FSMRCC.

For OH radical, we start with RHF of hydroxide anion as vacuum and choose the degenerate $\pi$ HOMOs as active orbitals. Removal of electron from these active orbitals results in doublet ($^2\Pi$) state of OH radical. It is seen from the polarizability results that the orbital relaxation effects in OH radical are also marginal.

Table 4.1: Polarizabilities of OH, HCOO and OOH radicals

| Molecule | State | | CVA-FSMRCCSD (Analytical) | FF-FSMRCCSD (energy) | FF-FSMRCCSD (dipole) |
|---|---|---|---|---|---|
| OH | $^2\Pi$ | $\alpha_{zz}$ | 6.61 | 6.0 | 6.1 |
| HCOO | $^2B_2$ | $\alpha_{zz}$ | 16.53 | 15.1 | 15.8 |
| | $^2A_2$ | $\alpha_{zz}$ | 16.68 | 15.2 | 16.0 |
| OOH | $^2A_2$ | $\alpha_{xx}$ | 15.01 | 13.9 | 14.6 |
| | | $\alpha_{yy}$ | 7.34 | 6.8 | 7.1 |
| | $^2A_1$ | $\alpha_{xx}$ | 12.52 | 11.9 | 12.3 |
| | | $\alpha_{yy}$ | 7.77 | 7.4 | 7.5 |

All results are in atomic units.

Removal of electron from RHF configuration of formate anion results in HCOO radical in its ground state ($^2B_2$) which strongly interacts with the closely lying excited state ($^2A_1$). The polarizability results for these states along the H-C direction are compared with the finite field method. The orbital relaxation effects are more prominent in this case. However, the trend in the two states is unaffected by the relaxation effects.

For polarizability calculations of OOH radical, we start with the RHF of hydroperoxide anion as vacuum. Removal of an electron from one of the last two occupied orbitals results in near-degenerate states ($^2A_2$ and $^2A_1$) of OOH radical. The polarizabilities along orthogonal directions ($x$ and $y$) for these states are reported in table. The orbital relaxation effects are important in this case as observed from the deviations of the analytical results from the corresponding finite field results. However, the difference between the polarizabilities of ground and excited states in both the directions is only marginally altered by orbital relaxation.

### 4.3.2 Electron attached states

We now discuss the analytical results for polarizabilities for CH, SiH and NO radicals. The geometries, basis sets and the choice of vacuum and active orbitals in all these radicals are as mentioned in the earlier chapter.

Table 4.2: Polarizabilities of CH and SiH radicals along molecular axis.

| Molecule (State) | CVA-FSMRCC (Analytical) | UGA-CCSD[a] (Finite Field) | Finite Field (energy) | Finite Field (dipole) |
|---|---|---|---|---|
| CH ($^2\Pi$) | 15.86 | 16.22 | 16.2 | 15.9 |
| SiH($^2\Pi$) | 37.44 | 38.81 | 38.3 | 38.0 |

[a] See [10]

All results are in atomic units.

### ***CH and SiH radicals***

Table 4.2 gives polarizabilities of CH and SiH radicals along the direction of molecular axis. We also present the (finite field) UGA-CCSD [10] polarizabilities of these molecules for comparison. We have also presented energy based and dipole moment based FF-FSMRCCSD calculations. The orbital relaxation seems to slightly increase the polarizability values as seen from the result. The effect is however, only marginal.

### ***NO radical***

Polarizabilities of NO are given in Table 4.3. We have reported the results for ground state ($^2\Pi$) and first excited state ($^2\Sigma$). The calculations have been done keeping the molecular axis along $z$ direction. We compare the ground state polarizability components with CCSD and CCSD(T) results [11] obtained using finite field method at the same geometry and basis set. We also present the experimental result [12, 13] for mean polarizability of the ground state. It may be noted that that application of external electric field in the direction perpendicular to N-O axis, results in loss of degeneracy of the $^2\Pi$ LUMO of NO as was also observed by Medved *et. al.* [11] in their calculations. This is what one can infer from the theoretical results reported in the table. The orbital relaxation is only marginal in this case as seen from the CCSD and CCSD(T) results.

No results for excited state ($^2\Sigma$) of NO are available for comparison. We present energy based and dipole moment based FF-FSMRCCSD calculations. We see that for excited state also, the analytical results agree with the trend observed in finite field methods.

Table 4.3: Polarizabilities of NO radical

| State | Method | $\alpha_{zz}$ | $\alpha_{xx}$,$\alpha_{yy}$ | $< \alpha >$ | $\Delta\alpha$ |
|---|---|---|---|---|---|
| $^2\Pi$ | CVA-FSMRCC | 14.72 | 9.96<br>8.90 | 11.19 | 5.29 |
| | CCSD[a] | 15.29 | 10.08<br>9.10 | 11.49 | 5.70 |
| | CCSD(T)[a] | 15.34 | 10.21<br>9.22 | 11.59 | 5.62 |
| | Experimental[b] | | | 11.518<br>±0.013 | |
| $^2\Sigma$ | CVA-FSMRCC | 243.99 | 260.58 | 254.05 | -16.59 |
| | FF(energy) | 240.9 | 258.2 | 252.4 | -17.3 |
| | FF(dipole) | 242.2 | 258.4 | 253.0 | -16.2 |

[a] Obtained using finite field method. See [11].

[b] See [12, 13].

All results are in atomic units.

## 4.4 Conclusion

In this article, we have presented first implementation of CVA-FSMRCC method for obtaining analytically, polarizability of open-shell doublet radicals, which can be described by $(1,0)$ and $(0,1)$ Fock space sectors. The method involves three sets of amplitudes, namely, the normal Fock-space amplitudes, their first derivatives and the amplitudes of the perturbation independent $\Lambda$-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, even after neglecting contribution of the orbital relaxation.

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# *Chapter 5*

# Excited states properties: FSMRCC linear response method with constrained variational approach

## 5.1 Introduction

Excited states of molecules are of special interest to theoretical as well as experimental chemists. The molecular properties like dipole moments, polarizabilities in electronically excited (EE) states have caught special attention due to their importance in the field of molecular spectroscopy. However, the calculation of electronically excited states poses a challenge due to the near-importance of different configurations in these states. This near degeneracy of configurations in excited states demands the use of MR description in the wavefunction. Often the low-lying excited states of closed-shell system result from pre-dominance of single electron excitation from the occupied orbitals of RHF of ground state of the closed-shell system to the virtual orbitals. In terms of FSMRCC [1–8], this MR description of model space belongs to $(1, 1)$ sector of the FS. By definition, this is an IMS. The basic difference between IMS and CMS is the incompatibility of intermediate normalization [2–5] with the valence universality of the wave-operator $\Omega$ in case of IMS. However, the one hole-one particle FS problem belongs to a special type of IMS. It is complete within the active-hole and active-orbital valence spaces; and is referred to as QMS [9]. It was shown by Mukherjee [2] and Pal *et. al.* [5] that, although the intermediate normalization is not valid in $(1, 1)$ FS problem, there is a CMS-like simplification.

Apart from this, methods like EOM-CC [10–13], SAC-CI [14–19], MRCI [20–23], MR-MBPT [24–27] have also been used recently for excited state electronic structure calculations. It may however, be noted that unlike one-valence cases, the equivalence between EOMCC and FSMRCC is no more valid for two-valence problems like the cases of one hole-one particle FS problem. Moreover, while size-extensivity is maintained in FSMRCC, the same is not true for EOM-CC method as discussed by Bartlett [28] However, recently the similarity transformed (ST) EOM-CC method of Nooijen and co-workers [29, 30] is found to be size-extensive.

In this chapter, we present our computational development of CVA-FSMRCCSD method for excited state properties and present the preliminary implementation of the method for obtaining low-lying excited states of some closed-shell systems. In particular, we present our CVA-FSMRCCSD calculations for obtaining dipole moments and polarizabilities of water and carbon monohydride cation in their low-lying triplet states. Although the applications are preliminary, we would like to extend the method for more difficult cases like excited singlet states of molecules. Before presenting our results, we briefly review the formulation of effective Hamiltonian and partial decoupling of the triplet states from the singlet excited states in the next section. This will be followed by CVA formulation for excited states. At last, we discuss the results of our pilot applications using CVA-FSMRCCSD.

## 5.2 Effective Hamiltonian for excited states

The FSMRCC theory is already discussed in Chapter 1. In this section, we rewrite the algebra in the context of $(1,1)$ sector of FS and discuss the details from the CVA formulation point of view. The universal wave operator for EE problem is

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

Under SD approximation, the $T$ operator of every sector will contain only one-body and two-body operators. Following Mukherjee [2, 31], Sinha *et. al.* [3] and Pal *et. al.* [4] the above valence universal cluster operator satisfies Bloch equation.

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

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

$$(\tilde{H}_{\mathit{eff}})^{(1,1)}_{\mu\alpha,\nu\beta} = (H_{\mathit{eff}})^{(1,1)}_{\mu\alpha,\nu\beta} + (H_{\mathit{eff}})^{(0,1)}_{\mu,\nu}\delta_{\alpha,\beta} + (H_{\mathit{eff}})^{(1,0)}_{\alpha,\beta}\delta_{\mu,\nu} + H^{(0,0)}_{\mathit{eff}} \tag{5.3}$$

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

$$P^{(k,l)} H\Omega - \Omega\tilde{H}_{\mathit{eff}} P^{(k,l)} \quad = \quad 0; \forall k, l = 0, 1 \tag{5.4}$$

$$Q^{(k,l)} H\Omega - \Omega\tilde{H}_{\mathit{eff}} P^{(k,l)} \quad = \quad 0; \forall k, l = 0, 1 \tag{5.5}$$

The normal ordering in the anasatz leads to SEC resulting in decoupling of lower valence sector equations from the higher ones. It was shown by Mukherjee [2] 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.

$$P^{(1,1)}\Omega P^{(1,1)} \neq P^{(1,1)} \tag{5.6}$$

Applying of Wick's theorem [32–34] on Eq. (5.4) and simplifying, one can write

$$P^{(k,1)}\widehat{H\Omega}P^{(k,l)} = P^{(k,l)}(\widehat{\Omega^{(k,l)}\tilde{H}}{}^{(k,l)}_{\mathit{eff}}P^{(k,l)} + P^{(k,l)}[\tilde{\Omega}^{(k,l)} - \widehat{\Omega^{(k,l)}]H}_{\mathit{eff}}P^{(k,l)} \tag{5.7}$$

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 $\widehat{\Omega^{(k,l)}\tilde{H}}_{\mathit{eff}}$ or $\widehat{\Omega^{(k,l)}H}_{\mathit{eff}}$. For $(1,1)$ sector problem, the only non-vanishing terms could appear only through the product of $T_1^{(1,1)}$ and $T_1^{(0,0)}$ operators. However, since $T_1^{(1,1)}$ 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

$$P^{(1,1)}\tilde{H}^{(1,1)}_{\mathit{eff}}P^{(1,1)} = P^{(1,1)}H\Omega P^{(1,1)} \tag{5.8}$$

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 $T_1^{(1,1)}$. Thus, although the FSMRCCSD wavefunction consists of $T_1^{(1,1)}$ amplitudes, these are not at all required for evaluation of excitation energies and derivatives. 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. The antisymmetrized $H_{\mathit{eff}}^{(1,1)}$ and $T^{(1,1)}$ can be explicitly expressed in terms of non-antisymmetrised parts. These lead to direct and exchange type $H_{\mathit{eff}}^{(1,1)}$ as well as $T^{(1,1)}$. We indicate them as $(H_{\mathit{eff}}^{dir})^{(1,1)}$, $(H_{\mathit{eff}}^{exc})^{(1,1)}$, $T^{dir(1,1)}$ and $T^{exc(1,1)}$ respectively. Obviously, the equations for $T^{(1,1)}$; i.e. $Q^{(1,1)}H\Omega - \Omega\tilde{H}_{\mathit{eff}}P^{(1,1)}$ will also be of direct and exchange types respectively. If $\{i, j\}$ are hole indices and $\{a, b\}$ are particle indices, the matrix element of a general direct type of skeleton has form $< i(1)b(2)|(\overline{Z})|a(1)j(2) >$ whereas the one for the exchange type will have form $< i(1)b(2)|(\overline{Z})|j(1)a(2) >$, where, $(\overline{Z})$ may be $H_{\mathit{eff}}^{(1,1)}$ or $T^{(1,1)}$ or skeleton of projected Bloch equations. The equations for $(H_{\mathit{eff}}^{exc})^{(1,1)}$ and $T^{exc(1,1)}$ are completely decoupled from the corresponding equations in the direct block. The direct block, however, depends on the effective Hamiltonian and the cluster amplitudes of exchange type. Thus in addition to SEC, there is further decoupling of exchange block from the direct one. After spin adaptation, effective Hamiltonians for singlet and triplet excited states are obtained, the matrix elements of which, can be written as

$$\begin{aligned}(H_{\mathit{eff}}^{singlet})^{(1,1)}_{\mu\alpha,\nu\beta} &= (H_{\mathit{eff}}^{exc})^{(1,1)}_{\mu\alpha,\nu\beta} - 2(H_{\mathit{eff}}^{dir})^{(1,1)}_{\mu\alpha,\nu\beta} \\ &\quad +(H_{\mathit{eff}})^{(0,1)}_{\mu,\nu}\delta_{\alpha,\beta} + (H_{\mathit{eff}})^{(1,0)}_{\alpha,\beta}\delta_{\mu,\nu} + H_{\mathit{eff}}^{(0,0)} \qquad (5.9)\end{aligned}$$

and

$$\begin{aligned}(H_{\mathit{eff}}^{triplet})^{(1,1)}_{\mu\alpha,\nu\beta} &= (H_{\mathit{eff}}^{exc})^{(1,1)}_{\mu\alpha,\nu\beta} \\ &\quad +(H_{\mathit{eff}})^{(0,1)}_{\mu,\nu}\delta_{\alpha,\beta} + (H_{\mathit{eff}})^{(1,0)}_{\alpha,\beta}\delta_{\mu,\nu} + H_{\mathit{eff}}^{(0,0)} \qquad (5.10)\end{aligned}$$

where, the indices $\{\mu, \nu, \alpha, \beta\}$ are as defined in Eq. (5.3)

The triplet excited states can thus be obtained by simply solving upto the exchange type Bloch equations. The singlet states calculation is however, relatively more complicated as it requires the knowledge of direct as well as exchange parts of the effective Hamiltonian and cluster amplitudes. If the $H_{\mathit{eff}}^{(0,0)}$ contribution is dropped, one can directly obtain excitation energies of the corresponding states.

## 5.3 CVA-FSMRCCSD anasatz for excited states

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 type of terms. Energy of a $m$-th excited singlet state of a system is given by

$$E_m^{singlet} = \sum_{ij} \tilde{C}_{mi}^{singlet(1,1)} (H_{\mathit{eff}}^{singlet})_{ij}^{(1,1)} C_{jm}^{singlet(1,1)} \tag{5.11}$$

We construct Lagrangian for this state as

$$\begin{aligned}
\Im^{singlet} \quad = \quad & \sum_{ij} \tilde{C}_{mi}^{singlet(1,1)} (H_{\mathit{eff}}^{singlet})_{ij}^{(1,1)} C_{jm}^{singlet(1,1)} \\
& + P^{(1,1)} \Lambda^{dir(1,1)} [H\Omega - \Omega H_{\mathit{eff}}^{singlet(1,1)}]^{dir} P^{(1,1)} \\
& + P^{(1,1)} \Lambda^{exc(1,1)} [H\Omega - \Omega H_{\mathit{eff}}^{singlet(1,1)}]^{exc} P^{(1,1)} \\
& + P^{(0,1)} \Lambda^{(0,1)} [H\Omega - \Omega H_{\mathit{eff}}^{(0,1)}] P^{(0,1)} \\
& + P^{(1,0)} \Lambda^{(1,0)} [H\Omega - \Omega H_{\mathit{eff}}^{(1,0)}] P^{(1,0)} \\
& + P^{(0,0)} \Lambda^{(0,0)} [H\Omega - \Omega H_{\mathit{eff}}^{(0,0)}] P^{(0,0)} \\
& - E_m^{singlet} \left( \sum_{ij} \tilde{C}_{mi}^{singlet(1,1)} C_{jm}^{singlet(1,1)} - 1 \right)
\end{aligned} \tag{5.12}$$

The $\Lambda$ vectors and cluster amplitudes are obtained by making the Lagrangian stationary with respect to cluster amplitudes and $\Lambda$ vectors respectively. The eigen vectors are also obtained variationally. The cluster amplitudes are thus completely decoupled from the $\Lambda$ vectors. As discussed in the earlier chapters, there is a reverse SEC decoupling scheme for the $\Lambda$ vectors of various sector. Moreover, the decoupling scheme between direct and exchange type $\Lambda^{(1,1)}$ vectors is exactly in reverse order of $T^{(1,1)}$ amplitudes. Thus after solving for cluster amplitudes up to $T^{dir(1,1)}$, one has to solve for

$\Lambda^{dir(1,1)}$, then $\Lambda^{exc(1,1)}$ and so on up to vacuum sector, i.e. $\Lambda^{(0,0)}$. The singlet excited response properties are obtained as are in the case of doublet radicals, after solving for derivatives of cluster amplitudes and/or $\Lambda$ vectors required after the application of $(2n+1)$ and $(2n+2)$ rules in the derivative Lagrangian expression.

For triplet state calculations, one has to construct Lagrangian using triplet state effective Hamiltonian. Since, the triplet states are independent of direct type of amplitudes, the Lagrangian for a specific triplet state is much simpler as it contains no contribution from the direct type of equations.

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

$$E_m^{triplet} = \sum_{ij} \tilde{C}_{mi}^{triplet(1,1)} (H_{\mathit{eff}}^{triplet})_{ij}^{(1,1)} C_{jm}^{triplet(1,1)} \tag{5.13}$$

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

$$\begin{aligned}
\Im^{triplet} \;=\; & \sum_{ij} \tilde{C}_{mi}^{triplet(1,1)} (H_{\mathit{eff}}^{triplet})_{ij}^{(1,1)} C_{jm}^{triplet(1,1)} \\
& + P^{(1,1)} \Lambda^{exc(1,1)} [H\Omega - \Omega H_{\mathit{eff}}^{triplet(1,1)}]^{exc} P^{(1,1)} \\
& + P^{(0,1)} \Lambda^{(0,1)} [H\Omega - \Omega H_{\mathit{eff}}^{(0,1)}] P^{(0,1)} \\
& + P^{(1,0)} \Lambda^{(1,0)} [H\Omega - \Omega H_{\mathit{eff}}^{(1,0)}] P^{(1,0)} \\
& + P^{(0,0)} \Lambda^{(0,0)} [H\Omega - \Omega H_{\mathit{eff}}^{(0,0)}] P^{(0,0)} \\
& - E_m^{triplet} \left( \sum_{ij} \tilde{C}_{mi}^{triplet(1,1)} C_{jm}^{triplet(1,1)} - 1 \right)
\end{aligned} \tag{5.14}$$

The common parts Eq. (5.12) and Eq. (5.14) apparantly similar. Although, both these contain the $\Lambda^{exc(1,1)}$ vectors, they are different for singlet and triplet states; firstly, due to the different spin multiplicities of effective Hamiltonian and secondly, due to coupling of the $\Lambda^{exc(1,1)}$ amplitudes with $\Lambda^{dir(1,1)}$ (and indirectly with $T^{dir(1,1)}$ amplitudes) in Eq. (5.12), which is unlike (5.14). Analogously, the lower sector $\Lambda$ amplitudes are also different for singlet and triplet states and are also different from the corresponding amplitudes for ionized or electron-attached states and the ground state. It is however, interesting to notice that, the homogeneous parts of the linear equations for $\Lambda$ vectors are same for a given sector, irrespective of the desired state. The difference comes only in the inhomogeneous parts of the equations where, the coupling terms from the higher sectors appear. The $\Lambda$ equations of various sectors for triplet-state calculations are relatively simpler than the ones for the corresponding singlet states. Hence, taking into account, the computational considerations, we have developed the code for computing triplet excited states of molecules with closed-shell ground state. We therefore, write the simplified expressions for first and second order properties (after application of the $(2n+1)$ and $(2n+2)$ rules) for triplet states only.

$$\begin{aligned}
\Im_{\mathit{opt}}^{triplet(1)} &= \left(\tilde{C}^{triplet(1,1)(0)} H_{\mathit{eff}}^{triplet(1,1)(1)}{}_{\Omega^{(0)}} C^{triplet(1,1)(0)}\right)_{m,m} \\
&\quad + P^{(1,1)}\Lambda^{exc(1,1)}[H^{(1)}\Omega - \Omega H_{\mathit{eff}}^{triplet(1,1)(1)}{}_{\Omega^{(0)}}]^{exc}P^{(1,1)} \\
&\quad + P^{(0,1)}\Lambda^{(0,1)}[H^{(1)}\Omega - \Omega H_{\mathit{eff}}^{(0,1)(1)}{}_{\Omega^{(0)}}]P^{(0,1)} \\
&\quad + P^{(1,0)}\Lambda^{(1,0)}[H^{(1)}\Omega - \Omega H_{\mathit{eff}}^{(1,0)(1)}{}_{\Omega^{(0)}}]P^{(1,0)} \\
&\quad + P^{(0,0)}\Lambda^{(0,0)}H^{(1)}\Omega P^{(0,0)}
\end{aligned} \tag{5.15}$$

$$\begin{aligned}
\Im_{\mathit{opt}}^{triplet(2)} &= \left(\tilde{C}^{triplet(1,1)(0)} H_{\mathit{eff}}^{triplet(1,1)(2)}{}_{\Omega^{(1)}} C^{triplet(1,1)(0)}\right)_{\mu\mu} \\
&\quad + P^{(1,1)}\Lambda^{exc(1,1)(0)}[H^{(2)}\Omega^{(0)} + H^{(1)}\Omega^{(1)} - (\Omega^{(0)}H_{\mathit{eff}}^{triplet(1,1)})_{\Omega^{(1)}}^{(2)}]^{exc}P^{(1,1)} \\
&\quad + P^{(0,1)}\Lambda^{(0,1)(0)}[H^{(2)}\Omega^{(0)} + H^{(1)}\Omega^{(1)} - (\Omega^{(0)}H_{\mathit{eff}}^{(0,1)})_{\Omega^{(1)}}^{(2)}]P^{(0,1)} \\
&\quad + P^{(1,0)}\Lambda^{(1,0)(0)}[H^{(2)}\Omega^{(0)} + H^{(1)}\Omega^{(1)} - (\Omega^{(0)}H_{\mathit{eff}}^{(1,0)})_{\Omega^{(1)}}^{(2)}]P^{(1,0)} \\
&\quad + P^{(0,0)}\Lambda^{(0,0)(0)}[H^{(1)}\Omega^{(1)} + H^{(0)}\Omega_{\Omega^{(1)}}^{(2)}]P^{(0,0)} \\
&\quad + 2\sum_{ij}\tilde{C}_{mi}^{triplet(1,1)(1)} H_{\mathit{eff}}^{triplet(1,1)(0)} C_{jm}^{triplet(1,1)(1)} \\
&\quad - 2E_m^{(0)}\sum_{i}\tilde{C}_{mi}^{triplet(1,1)(1)} C_{im}^{triplet(1,1)(1)}
\end{aligned} \tag{5.16}$$

The subscripts $\Omega^{(0)}$ and $\Omega^{(1)}$ indicate that the 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 $\Lambda$-vectors.

## 5.4 Results and Discussion

We now present some preliminary applications of CVA-FSMRCCSD method for excited state properties. In particular, we present the results for the lowest excited triplet states of water and CH$^+$. For finite field calculations, (denoted by FF-FSMRCC in the corresponding tables), we have performed the calculations for $\pm 0.001$ a.u. as the values for external fields. Finite field polarizabilities have been calculated as first order numerical derivatives of analytical dipole moments evaluated at the above field values.

### 5.4.1 Excited state properties of water

Low-lying excited states of water exhibit strong MR character. Hence, we have chosen this system for testing the efficiency of CVA-FSMRCCSD method. To test the efficacy of the method, we report the dipole moment and polarizability results for low-lying triplet states of water evaluated at ground state geometry. We also report the results for $^3B_1$ state obtained using the $^3B_1$ state geometry optimized by Urban and Sadlej [35] In particular, we report the results for the components along the $C_{2v}$ axis. Calculations for both the sets have been performed using Sadlej basis set.

### *Excited state properties at ground state geometry*

Analytical dipole moments and polarizabilities of water along the $C_{2v}$ axis for the four lowest excited triplet states are reported in Table 5.1. Sadlej basis set was used for the calculation. The RHF ground state electronic configuration of water is

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

The orbitals $1b_1^2$ and $3a_1^2$ are the highest and second highest occupied MO which are close-lying in energy. Similarly, the the orbitals $3sa_1^0$ and $3pb_2^0$ are the near-degenerate LUMOs. We choose these orbitals as active. The excitations $3a_1 \rightarrow 3sa_1$, $3a_1 \rightarrow 3pb_2$, $1b_1 \rightarrow 3sa_1$ and $1b_1 \rightarrow 3pb_2$ result in the lowest triplet states of water, namely, ${}^3A_1$, ${}^3B_2$, ${}^3B_1$ and ${}^3A_2$ respectively.

Table 5.1: Dipole moments and polarizabilities of water in low-lying excited states

| State | $\mu_z$ (CVA-FSMRCCSD) | $\mu_z$ (FF-FSMRCCSD) | $\alpha_{zz}$ (CVA-FSMRCCSD) | $\alpha_{zz}$ (FF-FSMRCCSD) |
|---|---|---|---|---|
| ${}^3A_1$ | -0.803 | -0.855 | 76.49 | 81.0 |
| ${}^3B_2$ | -0.727 | -0.615 | 38.85 | 41.1 |
| ${}^3B_1$ | -0.665 | -0.710 | 59.34 | 70.4 |
| ${}^3A_2$ | -0.562 | -0.444 | 39.62 | 42.2 |

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

The negative sign in the dipole moment values for all the states indicates the change in the orientation of the dipole moment in each state, with respect to the ground state. The analytical results for all the states are observed to differ significantly from the corresponding FF results. This may be due to two reasons; firstly, due to relaxation of orbitals in presence of external perturbation, which has been neglected in the analytical calculations and secondly due to poor description of different states at same geometry.

However, an interesting trend is still seen in the results. For example, with respect analytical (CVA-FSMRCCSD) results for dipole moment, the dipole moment values (magnitudes) are lowered for $A_1$ and $B_1$ states in case of FF method. On the other hand, for the $A_2$ and $B_2$ states, the FF method overestimates the dipole moments when compared with the corresponding analytical results.

The deviation of FF polarizabilities from the corresponding analytical results is, however, only marginal except for the ${}^3B_1$ state. The FF method is observed to slightly overestimate the polarizability as compared to the corresponding analytical (CVA-FSMRCCSD) values.

### *The lowest excited triplet state*

The dipole moment and polarizability ($C_{2v}$ component) for the lowest triplet state, i.e. the ${}^3B_1$ state have been presented in Table 5.2. The optimized geometry for ${}^3B_1$ state has been for this calculation. The choice of active orbitals is same as in case of the earlier calculations. We also present the CASSCF results [35] for comparison.

Table 5.2: Excited state dipole moment and polarizability of water

| State | Property | CVA-FSMRCCSD | FF-FSMRCCSD | CASSCF[a] |
|---|---|---|---|---|
| ${}^3B_1$ | $\mu_z$ | -0.536 | -0.484 | -0.416 |
| | $\alpha_{zz}$ | 51.05 | 48.0 | 62.4 |

[a] See [35].

All results are in atomic units.

Correlation is seen to increase the magnitude of the dipole moment. The deviation of FF results from the analytical results shows trend similar as observed in the earlier calculation. The deviation is, however, less significant in this case. The effect of geometry change with respect to the ground state can be observed from the comparison of the CVA-FSMRCCSD results in Table 5.2 with the corresponding values in the Table 5.1. The dramatic reduction in the deviation of FF polarizability from the analytical value clearly indicates the prominent relaxation in the orbitals due to geometry change. is only marginal as compared to the correlation effect. However, the relaxation is seen to decrease the dipole moment slightly.

### 5.4.2 Excited state properties of carbon monohydride cation

Table 5.3 presents excited state properties of carbon monohydride cation. In particular, we present the analytical dipole moment and components of polarizabilities for the triplet state formed by ${}^1\sigma^+ \rightarrow {}^1\pi$ transition. The analytical as well as finite field FSMRCC calculations were performed using Sadlej basis set. The geometry as reported by Olsen et. al. [36] has been used for the calculation. We also present the CCSD and Full CI results reported by Kállay and Gauss [37] for comparison.

Table 5.3: Dipole moment and polarizabilities of carbon monohydride cation in lowest excited triplet state

| State | Property | CVA-FSMRCCSD | FF-FSMRCCSD | CCSD$^a$ | FCI$^a$ |
|---|---|---|---|---|---|
| $({}^1\sigma^+ \rightarrow {}^1\pi)$ triplet | $\mu_z$ | 0.434 | 0.399 | | |
| | $\alpha_{zz}$ | 9.041 | 7.77 | 8.269 | 8.327 |
| | $\alpha_{xx} = \alpha_{yy}$ | 5.278 | 5.84 | 5.754 | 5.690 |

$^a$ See [37].

All results are in atomic units.

In order to obtain the desired excited state, we start with the RHF of $CH^+$ as vacuum and choose the HOMO $({}^1\sigma^+)$ as active hole. The two-fold degenerate LUMOs $({}^1\pi)$ are chosen as active particles.

The orbital relaxation is seen to decrease the dipole moment as seen from the finite field and analytical results. The effect of orbital relaxation is, however, only marginal.

The polarizability along the CH bond direction is slightly overestimated by CVA-FSMRCC as compared with the CCSD and Full CI result. The perpendicular components of polarizability, on the other hand, is underestimated slightly by CVA-FSMRCC. The orbital relaxation, although same, seems to be crucial in this case since, they are seen to alter the difference between the polarizability results as compared with the corresponding benchmark results, i.e. the Full CI.

## 5.5 Conclusion

In this chapter, we have presented our computational implementation of CVA-FSMRCC theory for electronically excited states of molecules and presented preliminary applications to obtain analytical dipole moments and polarizabilities of water and carbon monohydride cation in their lowest triplet excited states. From comparison of the results with the available benchmark results, it is clear that CVA-FSMRCC provides an efficient and cost-effective tool for obtaining the response properties. The scope of the method, however, will become broader only after further developments like extension to singlet excited states and incorporation of orbital relaxation corrections.

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# Epilogue

> "*It does not matter how beautiful your theory is, it does not matter how smart you are. If it does not agree with experiment, it's wrong.*"
>
> . . . *Richard Feynman*

In his above words, Richard Feynman has summarized the neccessary criteria, a theory must fulfil. The aim of a theoretical development should, therefore, be focused to aquire high degree of accuracy and its general applicability to wide range of chemical phenomena observed in the universe. The present work discussed development and applicability of a few highly accurate methods.

We presented our attempt to obtain magnetizabilities of closed shell systems using a sophisticated method like extended coupled-cluster. The extension of electric field response to magnetic field response is non-trivial as explained in the thesis. The preliminay applications in this context produced results under acceptable accuracy. However, the applicability of the extended coupled-cluster method will broaden only after incorporation of gauge-invariance technique like use of gauge-including atomic orbitals, individual gauge for localized orbitals, etc. which is a challenge in near future for theoretical chemists, in near future.

We have also presented the computational developments for a cost-effective technique to study response properties of near-degenerate systems and presented electric properties of doublet radicals and preliminary applications for electric field response of closed-shell molecules in their low-lying triplet excited states. The constrained variational response in Fock-space multi-reference coupled-cluster method has enabled to achieve the above implementations. This development has opened up a way to solve many incredible problems, although, computationally, the method is yet under development. The method, however, will become more general when the rigorous computational developments for more difficult cases like excited singlet states, double ionization, etc. will be done. In the present form also, the theory has wide range of applicability, since, it can be used to do magnetic response of open-shells and low-lying triplet states of molecules. The difficult tasks like geometry optimization of these near-degenerate systems using a highly correlated method like Fock-space multi-reference coupled-cluster method will also be possible in near future because of this development.

In short, the journey of the developments in theoretical methods goes on and on and breaks more and more bottle-necks. One would, therefore agree with Richard Feynman,

*"There's plenty room at the bottom"* . . .

# *Appendix A*

# The Geometries

All the geometries reported here are in atomic units.

| Molecule | Atom | X | Y | Z |
|---|---|---|---|---|
| OH | H | 0.00000 | 0.00000 | 1.85104 |
| | O | 0.00000 | 0.00000 | 0.00000 |
| OOH | H | -1.60075 | -1.66668 | 0.00000 |
| | $O_1$ | 1.27888 | -0.01807 | 0.00000 |
| | $O_2$ | -1.17802 | 0.12308 | 0.00000 |
| HCOO | H | 0.00000 | 2.96725 | 0.00000 |
| | C | 0.00000 | 0.88855 | 0.00000 |
| | $O_1$ | -1.98007 | -0.42700 | 0.00000 |
| | $O_2$ | 1.98007 | -0.42700 | 0.00000 |