Study of Response Properties using Coupled Cluster Method

Thesis submitted to the
University of Pune
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CERTIFICATE

This is to certify that the work presented in this thesis entitled, "**Study of Response Properties using Coupled Cluster Method**" by **Mr. Sumantra Bhattacharya**, for the degree of Doctor of Philosophy, was carried out by the candidate under my supervision in the Physical Chemistry Division, National Chemical Laboratory, Pune, PIN-411008, India. Any material that has been obtained from other sources has been duly acknowledged in the thesis.

Date: 08/01/2013

Place: Pune

Dr. Sourav Pal

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CERTIFICATE

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DECLARATION

I, Mr. Sumantra Bhattacharya hereby declare that the work incorporated in the thesis entiled “Studies of Response Properties using coupled cluster Approach” submitted by me to **University of Pune** for the degree of Doctor of Philosophy is original and has not been submitted to this or other University or Institution for the award of Degree or Diploma. Such material, as has been obtained from other sources has been duly acknowledged.

Date: 08/01/2013

Place: Pune

Sumantra Bhattacharya

For my parents, brother and family members

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List of abbreviations

AO	Atomic orbital
BO	Born-Oppenheimer
s	
BWPT	Brillouin-Weigner Perturbation Theory
CAP	Complex Absorbing Potential
CAP-CIP-FSMRCC	Complex Absorbing Potential-based Correlated Independent Particle in augmentation with Fock space multi-reference coupled cluster
CAP-FSMRCC	Complex Absorbing Potential-based Fock Space multi-reference coupled cluster
CAS	Complete Active Space
CAS-SCF	Complete Active Space Self Consistent Field
CBH	Campbell-Baker-Hausdroff
CC	Coupled Cluster
CCD	Coupled Cluster truncated at Doubles Excitation
CC-LR	Coupled Cluster Linear Response
CCRACNA	Complex Coordinate Real Axis Clamped Nuclei

CCSD	Coupled Cluster truncated at Singles Doubles Excitation
CCSD(T)	Coupled Cluster truncated at Singles Doubles Excitation with inclusion of partial Triples
CCSDT	Coupled Cluster truncated at Singles Doubles and Triples excitation
CCSDTQ	Coupled Cluster truncated at Singles Doubles Triples and Quadruple excitation
CEPA	Coupled Electron Pair Approximation
CPMET	Coupled-Pair Many-Electron Theory
CI	Configuration Interaction
CID/DCI	Configuration Interaction truncated at Doubles excitation
CISD	Configuration Interaction truncated at Singles Doubles excitation
CIP	Correlated Independent Particle
CSF	Configuration state function
CVA	Constrained Variation approach
DFT	Density Functional Theory
EA	Electron Affinity
ECC	Extended Coupled Cluster
EE	Excitation Energy

EOM-CC	Equations-of-Motion Coupled Cluster
FCI	Full Confugaration Interaction
FSMRCC	Fock Space Multireference Coupled Cluster
GVVPT	Generalized Van Vleck perturbation theory
HF	Hartree-Fock
HSMRCC	Hilbert Space Multi Reference Coupled Cluster
ICC	Internally Contracted Configurations
ic-MRCC	Internally Contracted Multi reference coupled cluster
IH	Intermediate Hamiltonian
IMS	Incomplete model space
IP	Ionization Potential
JM	Jezioroski and Monkhorst
MCSCF	Multi Configuration Self Consistent Field
MBPT	Many Body Perturbation Theory
Mk-MRCC	MuKherjee Multi Reference Coupled Cluster
MMCC	Method of moments coupled cluster
MO	Molecular orbital
MP2	Møller-Plesset second order Perturbation
MRBWCC	Multi-reference Brillouin-Weigner coupled cluster
MRCC	Multi Reference Coupled Cluster

MRCI	Multi Reference Configuration Interaction
MRCISD	Multi Reference Configuration Interaction truncated at Singles Doubles excitation
MRDFT	Multi Reference Density Functional Theory
MRexpT	Exponential multi reference wave function ansatz
MRPT	Multi Reference Multi Reference
POL-CI	Polarization configuration interaction
QDPT	Quasi Degenerate Perturbation Theory
RHF	Restricted Hartree-Fock
RMCC	Reduced Multi reference Coupled cluster
ROHF	Restricted Open Shell Hartee-Fock
RSPT	Rayleigh-Schrödinger Perturbation Theory
SAC-CI	Symmetry Adopted Cluster Configuration Interaction
SCF	Self Consistent Field
SEC	Subsystem Embedding Condition
SES	Smooth Exterior Scaling
SRCC	Single Reference Coupled Cluster
SSMRCC	State Specific Multi Reference Coupled Cluster
STEOM-CC	Similarity Transformed Equation-Of-Motion Coupled Cluster

SUMRCC	State universal Multi Reference Coupled Cluster
TCAP	Transformative Complex Absorbing Potential
TCCSD	Tailored coupled cluster singles doubles
UCC	Unitary Coupled Cluster
UHF	Unrestricted Hartee-Fock
VUMRCC	Valence Universal Multi reference Coupled Cluster
XCC	eXpectation value Coupled Cluster

Abstract

In this thesis we shall mainly focus on the calculation of properties using Fock space multi reference coupled cluster (FSMRCC) method. These properties include difference energies, shape resonance of electron molecule collision, geometry optimization and analytic gradient.

The state-of-the-art single-reference coupled-cluster (SRCC) [1-4] theory is one of the most accurate and widely used electronic structure methods for studying ground state structure, properties [5-7] and spectroscopy [8] of closed-shell molecules around equilibrium geometry. Apart from a high-level treatment of dynamic electron-correlation, the most attractive feature of SRCC method is that it is size-extensive [2] and separates correctly provided the reference state is also size-consistent, even at the truncated level, which is not true for truncated configuration interaction (CI) method [9].

SRCC theory, however, fails to describe properly the electron correlation when multiple determinants become equally important for the zeroth order description of the wave function. In general, in the case of quasi-degenerate situations, such as potential energy surfaces, bond-breaking or making regions, open shell systems and low-lying excited states of molecules, where multiple reference determinants become equally important, multi reference description becomes necessary.

MRCC theories can be divided into two classes, *e.g.*, single root MRCC, *e.g.*, state specific MRCC [10-15], and multi-root MRCC. We shall focus on second class. This theory is based on effective Hamiltonian defined over a

small model space. Diagonalizing the effective Hamiltonian within the model space [16, 17], we get multiple roots simultaneously. There are two effective Hamiltonian based MRCC theories, *viz*, the state-universal MRCC (SUMRCC) or Hilbert space multi reference coupled cluster (HSMRCC) [18] and the valence-universal MRCC (VUMRCC) or Fock space multi reference coupled cluster (FSMRCC) [19-23]. Both differ in the way the dynamic correlation is introduced and hence are suitable for different types of situations. HSMRCC is suitable for studying potential energy surface [24]. On the other hand, FSMRCC is suitable for the calculation of ionization potential [25], electron affinity [26] and excitation energy [22, 27]. In this thesis we shall focus on FSMRCC.

When there is a collision between electron and atom or molecule, the electron gets trapped into one of the virtual orbitals of the atom or a molecule. The compound system becomes quasi- bound and the wave function is not square integrable. The energy of the system is complex and can be written as:

$$E = E_r - i\frac{\Gamma}{2}$$

where, E_r and Γ are position, and width of the resonance, respectively [28, 29]. Thus we cannot apply normal bound state methods. To make the wave function square integrable, the analytical continuation of the Hamiltonian is achieved through complex scaling [29-31] or complex absorbing potential (CAP) [32]. FSMRCC method in augmentation with CAP method permits direct and simultaneous determination of both resonance position and width from the eigen values of an analytically continued Hamiltonian, and has been applied successfully to explain various atomic phenomena [32-34]. To study the shape resonance for electron-molecule collision we are going to adopt the aforesaid method, *i.e.*, FSMRCC method in augmentation with CAP method [35].

Response properties are obtained by taking derivative of energy with respect to perturbation. Derivative of energy can be calculated either numerically or analytically.

Calculation of response properties using SRCC method was initiated by Monkhorst [5]. Since the SRCC method is non variational [1], generalized Hellmann-Feynman theorem is not satisfied. As a result, the expression for first-order property in SRCC depends explicitly on first derivatives of the cluster amplitudes with respect to the external perturbation. Thus, it is necessary to calculate the cluster amplitude derivatives for all the modes of perturbation. For first-order properties, this apparent problem was overcome by Bartlett, *et. al.*, [36] using the idea of algebraic Z-vector method within CC frame work which was first applied by Schaefer [37] for configuration interaction method. However, application of Z-vector type of approach turns out to be tedious for higher-order properties, *e.g.*, hessian, polarizability.

A more elegant approach was proposed by Jørgensen and co-workers [38] based on constrained variation approach (CVA), using Lagrange undetermined multiplier. This method can be easily extended for higher order derivatives [38]. The incorporation of the constraint equation using Lagrange multiplier builds in a consequent (2n+1) rule [39] comparable with the stationary methods.

Study of molecular properties within the MRCC based methods is relatively recent. Originally Pal [40] proposed a straight forward derivative formulation of the effective Hamiltonian Bloch equation along the lines of Monkhorst [5]. However, since this involves first derivative of the wave function parameters in the first energy derivative. Subsequent to this Pal and co-workers formulated a constrained variation based approach to the MRCC problems [41, 42], where Bloch equations are introduced as constraints while making a specific root of the effective Hamiltonian stationary. At the same time Szalay [43] independently developed similar approach within the complete model space (CMS) for Hilbert space approach. However, the approach of Pal and co-workers [41, 42] used for general incomplete model space (IMS). Later, they made extensive development of theory within the FSMRCC approach to evaluate electric properties of excited and ionized states of suitable closed shell systems [44]. Thus, in addition to excited states doublet radicals have been studied

While the energy derivatives with respect to the electric fields has been studied [45-47] using Lagrange multiplier in the context of MRCC, there are almost no studies of such derivatives within the MRCC approach. In addition to Shape resonance, we will use this method to evaluate the analytic gradients of doublet radicals. This can be done within the one-valance Fock space approach. The thesis will also report optimization of geometry of excited states using one hole and one particle FSMRCC by calculating gradients numerically. The thesis is organized as follows:

First chapter: A general introduction is proposed leading to the subject matter of the thesis. Here, a brief overview of some of the basic concepts and developments in single reference coupled cluster theories are presented. Quasi-degenerate situations and their multi reference treatments are also highlighted. Introduction to computation of properties using numeric and analytic approach are discussed. We also introduce the idea of complex absorbing potential (CAP) and discuss the present status of CAP MRCC approach. We conclude the first chapter with the objectives and scope of the thesis.

Second chapter: The second chapter deals with shape resonance of electron-molecule collision. We present results of shape resonance arising from e^{-}-F_2, N_2O and CO collision. We have used correlated independent particle Fock space multi reference coupled-cluster augmented with complex absorbing potential (CAP-CIP-FSMRCC).

Third Chapter: The optimization of geometry is an extremely important task in chemistry. It is indeed challenging to find the geometries of excited states. No results are available using the MRCC method, which can describe the excited states accurately. In this chapter, we have optimized the geometry of molecules within the FSMRCC framework using numerical gradients. Low lying excited states are dominated by single hole, single particle excitations from ground state closed shell molecules have been described in this chapter. Excited state gradients are done by calculation of using finite field multi reference coupled cluster method. We also report adiabatic excitation energies to confirm the excited state geometries. We report excited state geometries of CH^+, H_2O, O_3 and HCHO.

Fourth Chapter: Development of analytic gradients within the FSMRCC. This is the first attempts of analytic gradients for FSMRCC. In this chapter we will give working equations for the analytic gradients of one valence problem.

Fifth Chapter: In this chapter we shall write general conclusion and scope of the thesis.

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CHAPTER I

Introduction

I.1. Overview of the thesis:

The goal of quantum chemistry which is derived from quantum physics is to explain various phenomena in chemistry like bonding, spectroscopy, molecular properties of atoms and molecules [1-3].

Application of quantum chemical techniques to study molecular properties has been developed significantly in last few decades, by involving either energy directly or by using derivative of energy. Several methods are available in literatures on diverse theoretical, conceptual and computational methods that have led to such progress [4–12]. Properties of molecule, *viz*, ionization energy, electron affinity, excitation energy, shape resonace study etc can be calculated by involving difference energy. The shape resonance study of electron-molecule collision which involves difference of energy has been studied in augmentation with complex scaling [13-16], complex absorption potential (CAP) [17, 18] and various other methods [19-21] by many bound state *ab initio* quantum mechanical methods [21-31].

Interpreting certain intermolecular behaviors study of electrical response is necessary. Response property calculation involes derivative of energy with respect to perturbation parameters. The electric and magnetic properties have been studied by several *ab initio* quantum mechanical methods [32-47]. The electrical and magnetic response properties have also been done earlier by Pal *et al*. [48], Pal and co-workers [49-55] by using highly accurate Fock space and Hilbert space multi reference coupled cluster framework. Other than external electric or magnetic field another perturbation parameter is change of nuclear coordinate. First derivative of energy with respect to coordinate is known as gradient. Gradient was first done by Pulay [56] within Hartree-Fock (HF) frame work. Now-a-days gradients can be calculated by several highly correlated *ab initio* methods [57-73]. Gradient is most challenging task to quantum chemists. On the other hand geometry optimization is the most important task to all class of chemists. Optimization of geometry requires first and second derivative of energy with respect to change of coordinate. Study of excited state geometry optimization has been very recent

The thesis will mainly focus on studying of the following two different properties:

1) Shape resonance.

2) Calculation of response properties, where the change of coordinate is the perturbation parameter.

Working on the first problem is challenging, because the particle is in quasi bound state, wave function is not square integrable. Hence, the bound state quantum theory is not applicable. However, with the help of complex scaling, complex absorption potential method, etc a free particle problem is converted into a bound state problem and bound state quantum chemical methods can be applied.

Working with various response properties has drawn attention, because it involves well-defined properties that are intrinsic to molecules, *e.g*. dipole moment, polarizability, hyper-polarizability, gradient, etc. It is important to understand these properties in order to explain chemical and physical phenomenon.

Based on the aim of the study, quantum chemistry can be further divided into molecular structure [2] and molecular dynamics [74]. Development of the molecular structure is very important, because the success of the molecular dynamics is dependent on the accuracy of molecular structure theory.

Hartree-Fock (HF) [2, 75-77] method is the simplest electronic structure method. It gives almost 95-99% of total energy. However, Hartree-Fock method fails to fulfill the requirements of chemists. Because in chemistry we are interested in the difference energies. To have correct difference energies, it is important to calculate both the quantities equally accurately. The small error in one can lead to wrong qualitative description. Addition to that HF does not include electron correlation of opposite spin, that’s why HF method fails to explain bond dissociation of closed shell molecules which fragment into open shell. There are several correlated many-body methods, *e.g*., configuration interaction (CI) [78], many-body perturbation theory (MBPT) [79-83] and coupled-cluster (CC) [84-87] theory. Correlation energy can also be calculated partly using density functional theory (DFT) [88, 89].

Full CI is exact and size extensive, but computationally very expensive. Truncated CI is neither size-extensive nor size-consistent.

MBPT is a very powerful method and often yields reasonably good results at low order of perturbation, but it suffers from the convergence problem.

DFT is computationally very easy, can even handle big molecules, but DFT cannot predict weak interactions accurately.

On the other hand, CC methods have drawn special attention because of size-extensivity and size-consistency (provided the reference is size consistent) even at the truncated level. This method is able to treat electron-correlation accurately. For these reason CC method serves as an efficient tool for studying molecular structure and property [90, 91]. The drawback of this method is that, it is computationally expensive for handling big systems (>50 atoms).

Analytical response approach within the CC framework was initiated by Monkhorst [90] and Bartlett and co-workers [91]. Later this method has explored as an efficient technique to study the energy derivatives.

For degenerate and quasi-degenerate states, where various determinants contribute equally, single reference description fails. Non-dynamic electron correlation, in general, is taken care through the linear combination of multi-determinants and hence, they are commonly known as multi-reference (MR) theory. Analogous to SR methods, this includes multi-reference configuration interaction (MRCI) [92], multi-reference Møller-Plesset perturbation method (MRMP) [93-96], multi-reference density functional theory (MRDFT) [97], multi-reference coupled cluster (MRCC) [98-100] theory etc. Multi reference methods include dynamical electron correlation in the similar way to their corresponding SR analogues.

MRCC method are further divided into two classes. First one describes a specific root and is known as the state-specific (SS) MRCC approach [101-107] and another is multi-root description. The multi root description methods are based on effective Hamiltonian approach [108]. Effective Hamiltonian is defined over a smaller space called model space. The diagonalization of the effective Hamiltonian within model space gives exact eigen values. Depending on the way the dynamic correlation is described [107, 109-117], these methods are further divided into Hilbert space (HS) [118] and Fock space (FS) [99, 113, 114, 119, 120] approach. In the HS approach, a state universal wave operator is introduced. The state universal wave operator contains different cluster operators for each of the determinants in the model space [99, 113, 114]. This method is widely applied for the study of potential energy surface (PES) [107a]. The HSMRCC method suffers seriously from intruder state problem, which arises when a determinant outside the model (reference) space is energetically almost degenerate to the state within the model space at some point on a potential energy surface. Intruder state problem can destroy the convergence of multi-reference, multi root procedure. It can even lead to unphysical features on computed potential energy surface. For multi reference problems Mukherjee *et al.* [101] developed state selective MRCC method for PES study. Their method is suitable from the point of view to overcome the intruder state problem. On the other hand for studying ionization [111], electron-attachment [121] and electronic excitation [117] of molecules Fock-space (FS) MRCC is suitable. This method is based on the concept of common vacuum and valence-universal wave-operator. Within Fock Space frame-work, the model space consists of different configurations, which are obtained by linear combination of electron occupancies among active orbitals. These occupancies of the active orbitals are denoted in terms of number of the active particles and active holes with respect to the vacuum. To eliminate intruder states in a computationally efficient manner Malrieu [108a] proposed effective FS Hamiltonian scheme. Meissner [107] implemented the method.

Single reference methods like equation-of-motion (EOM) CC (EOM-CC) [122-126], coupled cluster linear response (CC-LR) [127, 128], symmetry-adapted cluster configuration interaction (SAC-CI) [129, 130] etc. have also been developed to handle certain classes of quasi-degeneracy but within the single reference frame work. EOM-CC method is suitable for ionized, electron attached and excited states of molecules [131-139]. For one valance problem, *i.e.,* ionization potential (IP), electron affinity (EA) EOM-CC and FSMRCC are equivalent. However, such equivalency vanishes in higher valence sectors. Nooijen *et al.* [135, 136] have recently developed similarity transformed (ST) EOM-CC method. STEOM-CC method is size extensive. Jørgensen, *et al.*, [127] developed CC-LR method and is widely used for calculation of excitation energies. The EOM-CC and CC-LR excitation energies are identical. Within the EOM-CC framework derivative of energy for the calculation of property was formulated by Stanton [140]. Stanton and Gauss [141, 142] implemented derivative EOM-CC for calculation of property. Calculation of gradients within the STEOM-CC framework using a Lagrange undetermined multiplier was implemented by Nooijen *et al.* [143]. Still now energy derivatives in the context of MRCC methods is still a challenge. Pal [144] introduced a straight forward formulation for derivative of energy within MRCC framework. The method is based on Monkhorst's SRCC linear response approach [90]. Ajitha *et al.* [145, 146, 49, 50] developed computational algorithm for electrical response and applied for dipole moments of doublet radicals, low-lying excited states of molecules. In this approach derivative of energy need the evaluation of derivative cluster amplitude. In the SRCC framework, problem of derivative of amplitude was solved by incorporation of the Z-vector technique [147] or by using the constrained variational approach (CVA) [148, 149]. Szalay [67] has formulated CVA based energy derivative for EOM-CC, HSMRCC and FSMRCC within the complete model space (CMS). Pal, *et al*, [51, 150] proposed a formulation for derivative of energy within the FSMRCC [51b] and HSMRCC [51a] frame work, using Lagrange functional. Manohar *et al.* [53, 151] implemented CVA approach within FSMRCC framework for dipole moment and polarizability of doublet radicals and excited state molecules.

The focus of the thesis is mainly on calculation of response properties using Fock space multi-reference coupled cluster approach.

Electronic resonance is a well known phenomena of quantum theory. This phenomenon is observed when there is a collision between an electron and an atom or molecule. The electron gets trapped into a virtual orbital. The compound system becomes quasi-bound and the wave function loses its square integrability. Thus, the bound state methods cannot be used to describe the quasi bound problem. By introducing complex scaling [13-16] or complex absorption potential (CAP) [17, 18] the analytic continuation of the Hamiltonian can be achieved. Sajeev *et al*. [31] have introduced the correlated independent particle Fock space multi reference coupled cluster in augmentation with CAP (CAP-CIP-FSMRCC) to solve the resonance problem within the FSMRCC framework.

The organization of thesis is as follows:

First chapter: A general introduction is given leading to the subject matter of the thesis. In this chapter a brief overview of some of the basic concepts and developments in single reference coupled cluster theories are presented. Quasi-degenerate situations and their multi reference treatments are also highlighted. Introduction to computation of properties using numeric and analytic approach are discussed. We also introduce the idea of complex absorbing potential (CAP) and discuss the present status of CAP-FSMRCC approach. We conclude the first chapter with the objectives and scope of the thesis.

Second chapter: The second chapter deals with shape resonance of electron-molecule collision. We present results of shape resonance arising from

e^--F_2, N_2O and CO collision. We have used correlated independent particle Fock space multi reference coupled-cluster augmented with complex absorbing potential (CAP-CIP-FSMRCC).

Third Chapter: The optimization of geometry is an extremely important task in chemistry. It is indeed challenging to find the geometries of excited states. No results are available using the MRCC method, which can describe the excited states accurately. In this chapter, we have optimized the geometry of molecules within the FSMRCC framework using numerical gradients. Low lying excited states are dominated by one hole, one particle excitations of closed shell molecules have been described in this chapter. We also report adiabatic excitation energies to confirm the excited state geometries. We report excited state geometries of CH^+, H_2O, O_3 and HCHO.

Fourth Chapter: In this chapter we have developed the expressions for the analytic gradients using Fock space multi-reference coupled cluster (FSMRCC) theory. The expressions are given for one valance problem. Using Lagrange formulation equation for gradients are derived.

Fifth Chapter: In this chapter we shall write general conclusion and scope of the thesis. We shall discuss about the future prospects of the methods developed in the thesis.

I.2. Condition to be fulfilled by good theory:

The method should satisfy some basic conditions, such that it may be considered as a ‘theoretical model’ for electronic structure calculations. Pople *et al.* [152] proposed some criteria for a ‘theoretical model’ for electronic structure calculations and Bartlett [85] improved that. We shall briefly discuss them below:

1. The method should be independent of molecular systems, electronic configurations and symmetry.

2. The method should be invariant with respect to classes of transformation. Unitary transformations should not alter the orbital degeneracy.

3. The method should be **size-consistent**. A method is said to be size-consistent if energy obtained by its implementation on a system of several molecules at non-interacting limit is same as the sum of the energies obtained by separate implementations of the method on these molecules.

4. The method should be **size-extensive** which means energy of a strongly interacting many-electron system for a given potential should be approximately proportional to number of electrons in the system.

5. The method should be computationally cost effective and efficient.

The necessary and sufficient conditions for a theoretical method to be good are that, the method should fulfill size-consistency and size-extensivity criteria. Another most important criteria is efficiency and accuracy of the theoretical method. To develop a good theoretical model for calculating energy, these conditions should be satisfied not only in ground state as well as excited state and open shell systems also.

I.3. Size consistency and size extensivity:

I.3.A. Size consistency:

Pople, [152] and Bartlett [85] defined the term size-consistency. Size consistency of a method refers to its behavior. It is applied to a collection of N non-interacting monomers. Size-consistency is defined as additive separability of the energy during dissociation, *e.g.*, let us take a molecule AB, which dissociates into its fragment molecule A and B. If we calculate the energy of AB, A and B in a particular method, this method is can be designated as size-consistent, only when

$$E_{AB} = E_A + E_B \qquad (I.1)$$

is satisfied, and the corresponding wave function should be:

$$\Psi_{AB} = \Psi_A \Psi_B \qquad (I.2)$$

From the above explanation it is self defined that a self consistent method can predict qualitatively correct dissociation curve.

I.3.B. Size extensivity:

Another criterion for being a good theoretical method is size extensivity. Size extensivity is related to mathematical scaling of the energy of the system, with number of electrons [98, 109, 153, 154]. A theoretical method can be called size extensive, if the energy of a many electron system, calculated with the method, even in the presence of interactions, is proportional to the number of electrons N. The size extensivity is especially important for electron correlation methods. If a method is not size-extensive, the error in correlation energy shows either sub-linear or super-linear dependence on the number of electrons, *i.e.* size of the system. In the former case, fraction of the exact correlation energy recovered per electron decreases as the size of the system increases, at zero correlation energy in the limit $\mathrm{N} \to \infty$. In the later case the same fraction increases with the system size, leading to prediction of infinite correlation energy per electron as $\mathrm{N} \to \infty$. Therefore, all non-size-extensive methods show progressively unphysical behavior as size of the system increases. Size-extensive methods are considered to be particularly appropriate for large systems, as they strive to recover a roughly constant fraction of exact energy with increasing system size.

I.4. Second quantization:

Development of second quantization formalism, Feynman's diagrammatic representation [155], etc, accelerate the development of quantum field theory.

In Second quantization formalism the anti-symmetry property of wave function is converted into algebraic properties of certain operators. No new insight in physics is introduced by second quantization, but second quantization shows another way to treat the many-electron systems in a different manner. In second quantization much emphasis is given on one and two-electron integrals, *i.e.* $\langle i|\hat{h}|j\rangle$ and $\langle ij|\hat{g}|kl\rangle$ rather than from N electron wave function. Here we shall give a little overview of the method. For details please see ref. [155-157].

While treating the quantization of radiation fields Dirac introduced the concepts of second quantization formalism. It is applied in non-relativistic Schrödinger equation to describe matter field, then it became necessary to reformulate the quantum theory of identical many-particles, with an implicit incorporation of the symmetry or anti-symmetry principle associated with the particles. Here two terms are introduced, *viz*, quanta creation operator and quanta annihilation operators.

In the many-electron problem in quantum chemistry to describe second quantization complete orthonormal spin-orbitals $\{\chi_i(x)\}$ are considered. For each spin-orbital, $\chi_{i\,,}$ two operators, *viz.*, creation operator $\hat{a}_i^{\dagger}$ and annihilation operator $\hat{a}_i$. $\hat{a}_i^{\dagger}$ operates on an N-electron determinant which does not contain χ_i, it generates an (N+1)-electron system, not only that, it also contains χ_i orbital also. On the other hand $\hat{a}_i$ operates on an N-electron system, but here the N-electron determinant contains χ_i orbital, then it annihilates i$^{\text{th}}$ electron and generates an (N-1)-electron system, which does not contain χ_i. Mathematical representations of creation and annihilation operators are:

$$\hat{a}_i^{\dagger}|\chi_k \cdots \chi_l\rangle = |\chi_i \chi_k \cdots \chi_l\rangle \tag{I.3}$$

$$\hat{a}_i|\chi_i \chi_k \cdots\cdot \chi_l\rangle = |\chi_k \cdots\cdot \chi_l\rangle \tag{I.4}$$

NOTE: From now onward '^' will be dropped for operators, *e.g.*, $\hat{a}$ will be written as a

When there is no hole or particle, then that state is called vacuum state and is denoted by $|vac\rangle$ and postulated to exist with the following properties:

$$a_i^\dagger |vac\rangle = |\chi_i\rangle \tag{I.5}$$

$$a_i |\chi_i\rangle = |vac\rangle \tag{I.6}$$

$$\langle vac|vac\rangle = 1 \tag{I.7}$$

$$a_i |vac\rangle = \langle vac| a_i^\dagger = 0 \tag{I.8}$$

Since the spin-orbitals are orthonormal, that's why the creation and annihilation operators associated with an orbital are adjoint to each other and the determinants are anti-symmetric with respect to exchange of two orbitals. Creation operators of two orthonormal orbitals are anti commutator of each other. On the other hand, a pair of operators consisting of a creation and an annihilation operator follows the following anti commutation relation:

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = \left\{a_i^\dagger, a_j^\dagger\right\} = 0 \tag{I.9}$$

$$a_i a_j + a_j a_i = \left\{a_i, a_j\right\} = 0 \tag{I.10}$$

$$a_i^\dagger a_j + a_j a_i^\dagger = \left\{a_i^\dagger, a_j\right\} = \delta_{ij} \tag{I.11}$$

If $\mathrm{i} = \mathrm{j}$, then it can be proved that the term would not survive, *i.e.*, we cannot create or annihilate two electron in same spin orbital χ_i, which restates the Pauli's exclusion principle.

Let us have a set of creation operator and we start with vacuum state and successively creating electrons in different orbitals by using the set of creation operator. We can generate any determinant with a given number of electrons by using this string of creation operators. The linear vector space spanned by determinants with different number of electrons including vacuum state is known as Fock-space [158, 159]. Creation and annihilation operators can act within Fock space. Any determinant Φ_I in Fock-space can be represented by sequence of creation operators acting on the vacuum, *i.e.*

$$\Phi_I = a_i^\dagger a_j^\dagger a_k^\dagger ....|vac\rangle \tag{I.12}$$

The algebra of all linear operators on Fock-space is spanned by all possible distinct product operators $\{a_i^\dagger a_j^\dagger a_k^\dagger ... a_l a_m a_n ...\}$ are obtained by taking product of a string of creation $\{a_i^\dagger a_j^\dagger a_k^\dagger ...\}$ and annihilation operators $\{a_l a_m a_n ...\}$ [158].

In terms of second quantization electronic Hamiltonian can be represented as:

$$\begin{aligned} H_{el} = \sum_{i,k} \langle i|h|k\rangle a_i^\dagger a_k + \\ \frac{1}{2} \sum_{\substack{i,j \\ k,l}} \langle ij|g|kl\rangle a_i^\dagger a_j^\dagger a_k a_l \end{aligned} \tag{I.13}$$

Where, $\langle i|h|k\rangle$ and $\langle ij|g|kl\rangle$ are one electron and two electron integral terms, respectively and can be expressed as:

$$\begin{aligned} \langle i|h|k\rangle &= \int \chi_i^*(\vec{x}_1) h \chi_k(\vec{x}_1) d\vec{x} \\ \langle ij|g|kl\rangle &= \int \chi_i^*(\vec{x}_1) \chi_j^*(\vec{x}_2) h \chi_k(\vec{x}_1) \chi_k(\vec{x}_2) d\vec{x}_1 d\vec{x}_2 \end{aligned} \tag{I.14}$$

NOTE: From now onward '$\rightarrow$' will be dropped for operators, *e.g.*, $\vec{x}$ will be written as x

By using the normal ordering [81, 159] method and commutation rule, the matrix elements of second quantized operators between any two determinants can be evaluated. Normal ordering is defined as if the string of annihilation operators precede the creation operators, *e.g.* in Equation (I.13), the creation operators came first followed by the annihilation operators. By convention, the annihilation operators are written in the right of a creation operator, when they are associated with the same spin orbital and generate two terms, where the first term is known as contraction term and the second term consists of two creation-annihilation operators in anti-commutation form. The process of moving the annihilation operators to the right is continued for the left over operator sequences in both the terms until fully normal-order (full contraction) is achieved. When all the annihilation and creation operators are fully contracted, then the vacuum expectation value of a normal ordered operator will vanish, even the matrix elements are non-zero. Wick's theorem [159] explained the process in a simplified manner. Statement of Wick's theorem is, "any general operator sequence A is equal to sum of its normal ordered form {A} and normal-ordered form $\overbrace{\{A\}}$ of its all possible contracted terms." Thus, in terms of mathematics:

$$A = \{A\} + \overbrace{\{A\}} \qquad \text{(I.15)}$$

From Wick's theorem we can tell that the product of two normal-ordered operators X and Y are given as follows:

$$XY = \{XY\} + \overbrace{\{XY\}} \qquad \text{(I.16)}$$

Second term of right hand side of Equation (I.16) represents the normal-ordered form of product X and Y with all the possible contraction between them, excluding self-contractions. Normal ordering and Wick's theorem lead to diagrammatic representation of matrix element evaluation. A normal ordered Hamiltonian Equation. (I.13) can be diagrammatically represented by using a vertex to represent its matrix element, such as: $\langle ij|g|kl\rangle$. Normal ordered operator sequence associated with the matrix element can be represented by attaching certain labeled directed lines to the vertex. Annihilation operators are represented by upward directed lines coming into the vertex and the creation operators are represented by upward directed lines going out of the vertex.

The generalized Wick's theorem (Equation (I.16)) can be represented diagrammatically by putting X on top of Y. A contraction between X and Y is represented by a line joining an outgoing line on X, with an incoming line on Y with a matching orbital label. The second part of Equation (I.16) can be represented by drawing all possible connected graphs with lines connecting vertices of X and Y. These lines are called internal lines. Similarly, the first term can be represented by all disjoint diagrams without any connection between two vertices. The desired matrix element is obtained by selecting graphs with a set of external incoming lines matching the occupied orbitals on the left side determinant.

Concept of normal ordering, Wick's theorem and diagrammatic representation can easily be extended to hole-particle operators [81]. When normal ordering with respect to Φ_0 is considered, the electronic Hamiltonian Equation (I.13) can be expressed as:

$$
\begin{aligned}
&H_{el} = H_0 + H_N \\
&H_0 = \langle \Phi_0 | H_{el} | \Phi_0 \rangle \\
&H_N = \sum_{i,j} \langle i | h | j \rangle \{ a_i^\dagger a_j \} + \frac{1}{2} \sum_{\substack{i,j,\\k,l}} \langle ik | g | jl \rangle \{ a_i^\dagger a_k^\dagger a_l a_j \} \\
&\langle i | u | j \rangle = \langle i | h | j \rangle + \sum_{a \in \Phi} \left(\langle ia | g | ja \rangle - \langle ia | g | aj \rangle \right)
\end{aligned}
\tag{I.17}
$$

The curly bracket represents the normal-ordering of enclosed sequence of operators with respect to Φ_0. H_0 and H_N are vacuum expectation value and normal-ordered form of electronic Hamiltonian, respectively. In diagrammatic notation, the holes and particles are represented by downward and upward directed lines, respectively. Hole creation and annihilation operators are represented by hole lines terminating or originating from the operator vertex. Thus, the generalized Wick's theorem can be used to obtain diagrammatic representation of operator products and their matrix elements between any two arbitrary determinants.

The advantages of using second quantization method are as follows:

1) The anti-symmetry principle is easily incorporated into the picture.

2) The second quantized operators are suitable to describe those where number of electron changes, *e.g.*, ionization, electron affinity, etc, because the second quantized operators are independent of number of electrons.

3) Wick's theorem and associated diagrammatic representations simplify the implementation of the method and help to monitor their size-extensivity.

I.5. Hartree-Fock theory:

From assumptions of quantum mechanics the atoms and the molecules are in bound state formed by an equally attractive and repulsive electromagnetic interaction in the sea of electrons and heavy nuclei is moving.

To describe an atom or a molecule by quantum mechanics, it is necessary to solve the corresponding time-independent Schrödinger equation to determine wave-function (Ψ) [1, 2] of the system, which is:

$$H\left|\Psi\right\rangle = \varepsilon\left|\Psi\right\rangle \tag{I.18}$$

H is the Hamiltonian operator. H consists of kinetic energy of constituent particles and potential energy resulted out from various interactions among them. These interactions are of two types, one is attractive interaction, arises because of interaction between opposite charged particles, like attractive interaction between electron and nucleus and another is repulsive interaction, arises because of interaction between same charged particle, *e.g.*, electron-electron repulsion, nucleus-nucleus repulsion.

For a molecule consisting of M proton and N electrons. The Hamiltonian can be written as:

$$H = -\frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{\left\|r_i - R_A\right\|} + \sum_{\substack{i,j\\ i<j}}^{N}\frac{1}{\left\|r_i - r_j\right\|} + \sum_{\substack{A,B\\ A<B}}^{N}\frac{Z_A Z_B}{\left\|R_A - R_B\right\|} \tag{I.19}$$

The first two terms of right hand side of Equation (I.19) are the kinetic energy of the nuclei and electron, respectively. R_A and r_i are the spatial coordinates of nuclei A and electron i, respectively. The third term is electrostatic energy of attraction between electron i and nucleus A, Z_A is the charge of nucleus A. Among the five terms, first three terms represent attractive force, so come with a negative sign. On the other hand the last two terms are repulsive force, so sign is positive. Between the last two terms the first one is repulsive electrostatic force between electron i and j, the restriction $i < j$ is imposed to avoid double counting another option is to multiply by a factor $1/2$. Same is imposed for the last term, which arises because of electrostatic repulsion between nucleus A and B, of charge Z_A and Z_B. Ψ is the wave function of the system and is a function of space and spin coordinates of nuclei, denoting the combined space-spin coordinate of i$^{\text{th}}$ electron by $x_i = (r_i, \xi_i)$. Where, ξ_i, is the spin of i$^{\text{th}}$ electron. The N electron-M nuclear system wave function (Ψ) can be represented as:

$$\Psi(R_A, ..., R_M, x_1, ..., x_N)$$

Solution of the eigen value equation (I.18), gives stationary state energies and wave-functions. When no external perturbation is applied, then, the atoms and molecules are assumed to be in one of these stationary states, which are considered as the ground state.

Solution of Equation (I.18) is exactly solvable only for hydrogen atom, which contains only one electron and one nucleus, but it is not so simple for many electron systems. Thus, some approximations are necessary.

The nucleus is much heavier compared to electrons, so the velocity of the nuclei should be much lower than that of electrons. Thus, we can say that the motion of the nuclei can be frozen during electronic motion. This approximation is popularly known as the Born-Oppenheimer (BO) approximation [2, 160, 161]. Thus by using BO approximation we can drop the first and last term of equation (I.19). The rest term of the total Hamiltonian can be considered as electronic Hamiltonian (H_{el}), and can be expressed as:

$$H_{el} = \sum_{i=1}^{N} h(r_i) + \sum_{i<j}^{N} g\left(\left\| r_i - r_j \right\|\right) \tag{I.20}$$

Where, $h(r_i)$ and $g\left(\left\| r_i - r_j \right\|\right)$ are represented as:

$$\begin{aligned} h(r_i) &= -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{\left\| r_i - R_A \right\|} \\ g\left(\left\| r_i - r_j \right\|\right) &= \frac{1}{\left\| r_i - r_j \right\|} \end{aligned} \tag{I.21}$$

In Equation (I.20), the first term is known as one body operator and represents the coordinate of electron i, $h(r_i)$ is known as core operator and represents the Hamiltonian of an individual electron at the given nuclear configuration, no other interaction term is considered. The Second terms is the known as electrostatic repulsion force between electron i and j. It is a two-body operator. Solution of Equation (I.18) at a fixed nuclear geometry, with the above Hamiltonian, used in Equation (I.20) gives wave functions $\Psi_{el}(x_1,....,x_N;R_1,....,R_M)$ for different electronic states with corresponding electronic energies. $E_{el}(R_1,....,R_M)$. Addition of nuclear terms to electronic energy provides an potential energy surface (PES) [2, 161].

The BO approximation is important in quantum chemistry in the sense that it simplifies the complicated problem of involving many nuclei and electrons to many electron problem at a fixed geometry. By introducing the concept of PES, it serves to bring back the picture of molecule as formation of chemical bonds in between constituent atoms and of chemical reactions as occurring on an energy landscape.

The term x_i, depends not only on spatial coordinate, it is also dependent on spin part also. From Pauli's exclusion principle we know that, no two electrons can have same quantum number. Thus in a spatial orbital maximum two electrons can be accommodated. Since electrons are Fermions, that's why electrons are antisymmetric with respect to interchange of space-spin coordinates of any two electron. Mathematically antisymmetry can be represented as:

$$\Psi(x_1,x_2,....,x_N) = -\Psi(x_2,x_1,....,x_N) \tag{I.22}$$

Instead of above representation, we can represent same in determinant form, which is popularly known as Slater determinant, and can be written as:

$$\Psi(x_1,x_2,...,x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1)\chi_1(x_2).......\chi_1(x_N) \\ \chi_2(x_1)\chi_2(x_2).......\chi_2(x_N) \\ .. \quad\quad .. \quad\quad .. \\ .. \quad\quad .. \quad\quad .. \\ .. \quad\quad .. \quad\quad .. \\ \chi_N(x_1)\chi_N(x_2)....\chi_N(x_N) \end{vmatrix} \tag{I.23}$$

In short hand notation we can express a normalized Slater determinant as:

$$\Psi_I(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \left| \chi_i(x_1), \chi_j(x_2), ..., \chi_k(x_N) \right\rangle \qquad \text{(I.24)}$$

Here the normalization constant is included, and shows the diagonal elements of the determinant.

In BO approximation, we have shown that in Equation (I.19), an inter electronic repulsion term is present, making the solution of the equation complicated, by containing $\left(\left\| r_i - r_j \right\|\right)^{-1}$ term, which can never can be represented as: $(r_i)^{-1} - (r_j)^{-1}$. For this reason the Hamiltonian cannot be written as: $H = H_i + H_j$, to handle this term, we have to adopt further approximations.

The Hartree-Fock (HF) approximation [2, 75, 76] is a mile stone in electronic structure theory to describe an approximate solution of the electronic part of the Schrödinger equation. In the HF method the $1/r_{ij}$ term is handled very brilliantly.

The basis of the HF theory is that, the stationary states of many electronic systems, particularly in the ground state of a closed shell (All the electrons are paired) atoms and molecules can be described by single Slater determinant Equation (I.24)

$$\Psi_I(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) = \frac{1}{\sqrt{N!}} \left| \chi_i(\vec{x}_1), \chi_j(\vec{x}_2), ..., \chi_k(\vec{x}_N) \right\rangle$$

In this approximation each electrons are assumed to be independent of each other, *i.e.*, electrons are assumed to move in a spherically averaged inter electronic repulsion potential. This approximation takes care of $1/r_{ij}$ part. The

HF method is known as independent particle model. The spin orbitals are approximately varied by constraining them only to the extent that they remain orthonormal, *i.e.* $\langle \chi_a | \chi_b \rangle = \delta_{ab}$, until the minimum energy is achieved. In this way we get the best spin orbitals, which minimizes the energy. This procedure leads to integro-differential equations, which is known as Hartree-Fock equations. To make the electronic energy $\left(\langle \Phi_0 | H_{el} | \Phi_0 \rangle\right)$ stationary. In the HF equation the Fock matrix ($f(x)$) is consisted by two parts:

(1) one electron operator, it includes kinetic energy of electron (T_e) and potential energy of electron with nucleus (V_{ne}).

(2) two electron operator ($V_{HF}(x)$). The two electron operator takes care of the most important $1/r_{ij}$ term. The Hartree-Fock equation can be written as follows:

$$f(x)\chi_a(x) = \varepsilon_a \chi_a(x) \tag{I.25}$$

$$\begin{aligned} f(x) &= T_e + V_{ne} + V_{HF}(x) \\ &= -\frac{1}{2}\nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{\|r - R_A\|} + V_{HF} \end{aligned} \tag{I.26}$$

$$V_{HF}(x) = \sum_{j=1}^{N} J_j(x) + \sum_{j=1}^{N} K_j(x) \tag{I.27}$$

$$J_j(x)\chi_i(x) = \int dx' \frac{\chi_j^*(x')\chi_j(x')}{|x - x'|} \chi_i(x) \tag{I.28}$$

$$K_j(x)\chi_i(x) = \int dx' \frac{\chi_j^*(x')\chi_i(x')}{|x - x'|} \chi_j(x) \tag{I.29}$$

$f(x)$ is the Fock operator [2]. $V_{HF}(x)$ is the Hartree-Fock potential. $V_{HF}(x)$ consists of two parts: (1) The Coulomb term and (2) The exchange term.

The Coulomb term is expressed by $J_j(x)$. Expression of $J_j(x)$ is given in Equation (I.28). Physical significance of Coulomb term is that, it is a spherically averaged potential experienced by an electron due to motion of all the other electrons.

The exchange term is denoted as: $K_j(x)$. The expression of $K_j(x)$ is given in Equation (I.29). There is no counterpart in classical mechanics regarding the physical significance of exchange potential. Since wave function is antisymmetric in nature so the exchange term is introduced in quantum mechanics.

In the integro-differential HF method, Equation (I.25), $\chi_a(x)$ exists in the both side. Thus, to solve the equation iterative procedure is adopted [2]. To solve this equation, an initial guess of spin orbitals is used to calculate the approximate HF potential. Fock matrix is used to obtain a new set of spin-orbitals. This procedure is repeated until some self-consistency is achieved between successive iteration. That’s why this method is known as self consistent field (SCF) method.

When Equation (I.25) to Equation (I.29) are solved, yields an orthonormal set of spin orbitals. $(\chi_i, i = 1, 2, ..., \infty)$, with corresponding orbital energy ε_{i}. The N spin orbitals $(\chi_a, a = 1, 2, ..., N)$, with lowest energies are referred to as occupied orbitals (hole), and the remaining set of spin-orbitals

$\left(\chi_r, r = N+1,....,\infty\right)$, are referred to as unoccupied or virtual orbitals (particles). Slater determinant consists of occupied spin-orbitals is the HF wave-function that approximates a stationary state of the Hamiltonian.

The HF approximation is in good agreement for ground state of non-degenerate many-electron systems and equations are exactly solvable as non-linear integro-differential equations only for atoms [2]. For molecules, orbitals involved are centered at different nuclei. For this reason the explicit two-electron interaction term is difficult.

To overcome this problem, Roothan [77] introduced the concept of expansion of basis set functions, which is a finite set of spatial basis functions $\left\{\phi_\mu\left(r\right), \mu = 1,..,k\right\}$. Basis functions are introduced to expand the spatial part of the spin-orbitals, which converts an integro-differential form of HF equation into a matrix eigen value HF equation for the expansion coefficient. Using iterative SCF procedure the equations are solved. Based on different forms of spin orbitals, several varieties of HF methods came out, *e.g.*, restricted Hartee Fock (RHF) came into picture by imposing the restriction of spin-orbitals, obtained by associating different spin-functions to a set of spatial orbitals. The closed shell HF determinant is referred to as closed shell RHF method. In open shell systems unpaired electron(s) is present in the system and known as restricted open shell HF (ROHF) method. On the other hand, use of unrestricted set of orbitals results in unrestricted HF method. RHF or ROHF determinant is purely an eigen function of total spin operator S^2, whereas, UHF determinant is not in general.

The advantage of HF approximation is that it replaces the complicated many-electron problem to an independent particle picture by treating electron repulsion in a spherically average manner, leading to very popular molecular orbital (MO) theory, where electrons occupy different orbitals. This is the first accurate approximate method to approach modern quantum chemistry.

Although HF method gives 95-98% accurate exact ground state energy, but the interest of chemists are in taking the difference of energy, which leads to higher percentage of error. Other than this, there are some other draw backs of HF method. The drawbacks of the HF methods are as follows:

1) HF method cannot account for the instantaneous electron repulsion.

2) HF method is very good to explain the ground state energy and properties of molecules, but it fails to explain the excited state and quasi degenerate states of molecules.

A very good example, where HF theory fails is that, it wrongly predicts the ionization energy of nitrogen molecule; even qualitatively it fails to explain properly.

That’s why we have to search for better method.

I.6. Correlation energy:

As of our earlier discussion the energy obtained from HF method cannot give exact energy. Thus, there is a difference between exact energy and HF energy. This difference of energy is called as correlation energy.

$$E_{corr} = \varepsilon_0 - E_0 \qquad \text{(I.30)}$$

E_{corr}, ε_0, E_0 are correlation energy, exact energy and HF energy, respectively.

The correlation energy is responsible for optical and chemical properties and can be compared to binding energy of outer valance electrons. Before discussing details about properties of molecules we shall first discuss about the various methods to calculate the correlation energies. Configuration interaction (CI) [2, 78, 162], many body perturbation theory (MBPT) [79-83], coupled cluster (CC) theory [84-87, 163], density functional theory (DFT) [88, 89] are the commonly used technique to calculate the correlation energy.

In the next sub-sections we shall give an outline about the fully correlated methods. We can classify the methods available to calculate correlation energies in the following manner:

A) Variation method, *e.g.*, configuration interaction (CI) method, independent electron pair approximation (IEPA), coupled electron pair approximation (CEPA).

B) Perturbative method, *e.g.*, many-body perturbation theory (MBPT).

C) Neither variational, nor perturbative (non-variational, non-perturbative) method, *e.g.*, coupled cluster (CC) method.

I.6. A. Variational method: configuration interaction (CI) method:

Conceptually most simple method to calculate the correlation energy is configuration interaction (CI) method [2, 78, 162]. From HF theory we get a set of orthonormal orbitals as eigen functions of the Fock operator. For an N-electron system, the exact wave function can be obtained by a linear combination of many determinants configurations.

The CI wave function can be written as:

$$\Psi = \Phi_0 + \sum_{i,a} C_i^a \Phi_i^a + \sum_{\substack{a>b \\ i>j}} C_{ij}^{ab} \Phi_{ij}^{ab} + ... \qquad \text{(I.31)}$$

Here intermediate normalization, *i.e.*, $\langle \Phi_0 | \Psi \rangle = 1$ is assumed. Where Ψ is the CI wave function and Φ_0 is Hartree-Fock wave function or reference determinant. In Equation (I.31), $i, j,..,$ etc. denote the occupied orbitals, and $\mathrm{a}, \mathrm{b},..,$ etc. are virtual orbitals in reference determinant. Throughout the thesis $i, j,..,$ are denote occupied orbital and $\mathrm{a}, \mathrm{b},..,$ denote virtual orbital, unless until it is mentioned specifically. The constraints $a > b$, $i > j$ are imposed to avoid double counting. Here Φ_i^a is singly excited determinant, which is obtained by replacing occupied orbital χ_i in Φ_0 by an unoccupied orbital χ_a. Similarly, Φ_{ij}^{ab} is denoted as doubly excited determinant.

Using linear variation method to determine expansion coefficients is known to result in eigen value problem for the Hamiltonian matrix, defined over all the determinants [2]. Matrix elements of Hamiltonian between any two Slater determinants are evaluated by using Slater-Condon rules [2]. Full-CI (FCI) method includes all possible N electron excited determinants within a given basis. The lowest eigen value and eigenvector of full-CI (FCI) Hamiltonian matrix corresponds to the ground state, rest of the eigen values and eigenvectors correspond to different excited states. FCI is conceptually simple, size consistent and within a given basis set FCI gives exact solution of many electron problem. For large molecules, inclusion of N electron excited determinants is computationally very expensive. If we choose a small molecule with moderate size of basis set, the number of excited determinants rapidly increases, but it is also true that large basis set is necessary to obtain accurate correlation energy. That's why FCI is computationally impractical. So truncation up to a certain number of excited state determinants is necessary, but not truncation upto first excitation, because of Brioullin theorem [2]. CI method truncated up to any excitation may lead to loss of size extensivity and size consistency. General truncation scheme restricts excited determinants to only doubles or singles and doubles. The first one is known as configuration interaction doubles (CID/DCI) and the later one is configuration interaction singles and doubles (CISD). Truncated CI methods are suitable especially for ground state, because here the reference determinant is dominant and recover correlation energy significantly for small system within a given basis set [164]. However it fails as size of the system increases.

FCI is size consistent, but computationally very expensive, so it is better to choose truncated method, but truncation up to any excited states, leads to loss of size consistency. We can explain this in the following way:

Let us consider a molecule AB, consists of A and B. Assuming that the wave functions of AB, A, B obtained by CID method are Ψ_{AB}, Ψ_{A} and Ψ_{B}, respectively. CID would include up to two electron excitation. Whereas, the product $\Psi_{\mathrm{A}} \bullet \Psi_{\mathrm{B}}$would include up to four electron excitations, which indicates that, $\Psi_{AB} \neq \Psi_A \Psi_B$, as a corollary we can say also that $E_{AB} \neq E_A + E_B$. Thus, it is proved that CID is not a size-consistent method. Similarly we can generalize that any truncated CI is not size extensive.

Similarly, another criterion for being a good theoretical method is size extensivity, which is related to mathematical scaling of the energy of the system, with number of electrons [98, 153, 154].

Studies on truncated CI methods have shown that the percentage of exact correlation energy within a given basis is obtained in these methods decreases as the size of the molecule increases [1]. For this reason truncated CI methods loss size-extensivity.

CI being conceptually very simple method, but computationally very difficult. The energy obtained from truncated CI is found to show sub-linear dependence [2], with the number of electrons tends to infinity. Thus, any form of truncated CI cannot be considered as good theoretical model.

Significant development is observed for getting correlation energy by CI techniques and these methods avoid the exact diagonalization of the Hamiltonian matrix. The Slater determinants used in traditional CI are generally impure spin eigen functions. Due to spin-free nature of electronic Hamiltonian, using spin adapted N-electron functions referred to as configuration state functions (CSF) which is a very efficient technique [78, 162]. Various approaches have been developed for construction of spin-adapted CSF:

(i) Unitary group approach (UGA) method was developed by Paldus, *et al*. [165]. Here CSF is considered as basis of the irreducible representation space of an underlying unitary group [166]. Shavitt [167] implemented UGA using graphical representation of CSF.

(ii) Symmetric group approach (SGA) was introduced by Matsen [166] and Karwowski *et al.* [168, 169]. Here the CSF is constructed as basis for irreducible representation of N-electron permutation group S_N.

(iii) Iterative diagonalization technique developed by Davidson [170]. It is an alternative way to determine the eigen values and eigen vectors of the Hamiltonian matrix in CI method. By introducing matrix vector product with a trial vector, unnecessary step of complete diagonalization is avoided.

(iv) Roos [171] proposed a direct CI procedure. It is used very often to compute this product to avoid explicit construction and storage of Hamiltonian matrix elements.

(v) Siegbahn's [172] method involves combination of direct CI technique with a graphical UGA to achieve efficiency in large scale calculations.

I.6.B. Independent electron pair approximation (IEPA):

Since the Hamiltonian contains two particle interaction at most, the triples and higher excitations do not contribute directly to correlation energy. Singles contribution is absent due to Brillouin's theorem [2]. This suggests that total correlation energy can be written as sum of correlation energy from occupied pairs.

$$E_{corr} = \sum_{i<j} e_{ij}$$

with $$e_{ij} = \sum_{a<b} C_{ij}^{ab} \left\langle \Phi_0 \middle| H \middle| \Phi_{ij}^{ab} \right\rangle$$

We devise an approximate N electron problem into $\frac{\mathrm{N}(\mathrm{N}-1)}{2}$ two electron problem. This scheme is known as independent electron pair approximation (IEPA).

Sinanoğlu [173] and Nesbet [174] independently introduced this concept in quantum chemistry. Sinanoğlu [173] named it as many-electron theory (MET).

The IEPA is based on two approximations:

1) Neglect the pair coupling terms

2) Assuming the non-linear terms cancel with part of the energy terms

The IEPA wave-function and energy expressions are:

$$\left| \Psi_{ij} \right\rangle = \left| \Phi_0 \right\rangle + \sum_{a<b} C_{ij}^{ab} \left| \Phi_{ij}^{ab} \right\rangle \tag{I.32}$$

$$\begin{aligned} E &= \left\langle \Phi_0 \middle| H \middle| \Phi_0 \right\rangle + \sum_{a<b} C_{ij}^{ab} \left\langle \Phi_0 \middle| H \middle| \Phi_{ij}^{ab} \right\rangle \\ &= E_{HF} + e_{ab} \end{aligned} \tag{I.33}$$

From Equation (I.33) it is clear that the correlation energy obtained from this method is same as obtained by CID. Hence IEPA is often entitled as pair-at-a-time CI [2], but IEPA is computationally simpler than CID. It is apparently meant that the IEPA is an approximation of CI, but incorporating the coupling between different pairs concludes that it is an approximation to FCI. IEPA gives size-extensive results but it is not invariant to unitary transformation.

I.6.C. Coupled-electron pair approximation (CEPA):

Meyer [175] proposed and implemented the coupled-electron pair approximation (CEPA), by including the interactions between the pairs, but neglecting the non-linear terms.

In CEPA the expression of correlation energy is:

$$E_{corr} = \sum_{c<d} \left\langle \Phi_0 \middle| H \middle| \Phi_{ij}^{ab} \right\rangle C_{ij}^{ab} \tag{I.34}$$

There are several forms of CEPA [176-178]. Among them some give size-extensive results.

I.6.D. Perturbative method: many-body perturbation theory (MBPT):

Another useful approach to calculate the correlation energies of atoms and molecules is Many body perturbation theory (MBPT) [79-83]. The method is non-variational. It adopts perturbative approach. MBPT is classified into two types: Møller-Plesset (MP) [2] and Epstein-Nesbet (EN) [179] perturbation theories.

In MBPT approach the exact Hamiltonian H is partitioned into zeroth-order Hamiltonian, H_0 and a small term H' known as perturbation. Stationary states (Φ_I) and energies (E_I) of the zeroth-order Hamiltonian and the perturbation matrix elements $\left\langle \Phi_I \middle| H' \middle| \Phi_J \right\rangle$ are known. On the other hand the stationary states (Ψ_I) and energies (E_I) of the H have to determine in terms of these known quantities. Assuming that there exsists an one-to-one correspondence between stationary states and energies of H_0 and H, *i e*. there is a parameter λ, known as perturbation parameter, which varies from 0 to 1 and connects eigen values and eigen vectors of H_0 (for $\lambda = 0$) and H (for $\lambda = 1$). In perturbation theory (Ψ_I) and (ε_I) are obtained by expanding a Taylor series in the limit of $\lambda \to 0$, *i e*, zeroth-order Hamiltonian. One more assumption is that, the H_0 is chosen in such a manner that the perturbation is small enough for the Taylor series to be convergent. The reason for this assumption is that the first few terms in the expansion yields sufficiently accurate approximation to the exact values. In practice it is possible to satisfy these requirements only for ground state. That's why perturbation theory is applied mainly to calculate correlation energy of the ground state of closed shell systems. Generally H_0 is chosen as one electron operator, such that (Φ_I) are represented by determinants. When perturbative corrections to HF ground state and energies are to be calculated, H_0 is chosen as sum of Fock operators, *i e*, $H_0 = \sum_i f(i)$. This is called Møller Plesset (MP) partitioning scheme. Here Φ_0 is dominant determinant for ground state, E_0 is the zeroth order energy which is the sum of energies of occupied HF orbitals, and ($\Phi_I, I \neq 0$) are various excited determinants. Assuming that Zeroth-order ground state Φ_0 and the corresponding exact ground state Ψ_0 are intermediately normalized, *i e*, $\langle \Phi_0 | \Psi_0 \rangle = 1$. Difference between the exact ground state energy (ε_0) and zeroth-order energy (E_0) is denoted by $\Delta\varepsilon_0$ can be written as follows:

$$\varepsilon_0 - E_0 = \Delta\varepsilon_0 = \langle \Phi_0 | H' | \Psi_0 \rangle \quad \text{(I35)}$$

In perturbation theory, $\Delta\varepsilon_0$ and Ψ_0 are written as series of correction terms of increasingly higher order in perturbation.

$$\Delta\varepsilon_0 = \Delta\varepsilon_0^{(1)} + \Delta\varepsilon_0^{(2)} + \ldots + \Delta\varepsilon_0^{(n)} + \ldots. \quad \text{(I.36)}$$

$$\Psi = \Phi_0 + \Psi_0^{(1)} + \Psi_0^{(2)} + \ldots + \Psi_0^{(n)} + \ldots. \quad \text{(I.37)}$$

$$\Delta\varepsilon_0^{(n)} = \langle \Phi_0 | H' | \Psi_0^{(n-1)} \rangle \quad \text{(I.38)}$$

Here $\Delta\varepsilon_0^{(n)}$ and $\Psi_0^{(n)}$ are the n-th order energy and wave function correction for ground state respectively and contain n-th power perturbation of H'.

There are various methods available to solve the correction of energy and wave functions at various orders of perturbations. Brillouin-Weigner perturbation theory (BWPT) [81], Rayleigh-Schrödinger [79, 81, 82] perturbation theory (RSPT) are important among them.

In BWPT, the perturbation at any order is dependent on exact ground state energy E_0, which is unknown. Thus, one has to solve for total energy up to a certain order by iterative procedure [81]. The expression for $\Delta\varepsilon_0^{(n)}$ and $\Psi_0^{(n)}$ in BWPT are given below:

$$\Delta\varepsilon_0^{(n)} = \langle \Phi_0 | H' \left(\frac{Q_0}{E_0 - \Delta\varepsilon_0} \right)^{n-1} | \Phi_0 \rangle \quad \text{(I.39)}$$

$$\Psi_0^{(n)} = \left(\frac{Q_0}{E_0 - H_0} (H' - \Delta\varepsilon_0) \right)^{n} | \Phi_0 \rangle \quad \text{(I.40)}$$

On the other hand in RSPT, the quantities in the Equation (I.39) and Equation (I.40) are substituted in the Schrödinger equation. The terms of fixed power of V are then collected and solved for energies and wave functions of various orders.

In contrast to BWPT, these expressions contain only the known unperturbed ground state energy E_0 in the denominator of the resultants, that's why, can be applied directly without resorting to iterative procedure.

Brueckner [180] proved that RSPT with MP partitioning leads to size-extensive perturbation series. It was done for the first few orders in the context of infinite nuclear matter. Using diagrammatic approach, Goldstone [181] and Hugenholtz [182] showed that the term which have size-intensive, correspond to unlinked set of diagrams. It can be proved that the MP partitioned RSPT contains such unlinked diagrams mutually cancel at every perturbation order and leading to a size-extensive series, this is known as the linked diagram theorem. Kelly [183] applied the diagrammatic approach for atoms.

Applications of RSPT are based on RHF vacuum employ the Møller-Plesset (MP) partitioning scheme. The zeroth order Hamiltonian is a diagonal operator, expressed in terms of HF orbital energies, which simplifies the expressions for energy and wave function corrections and is known as Møller-Plesset perturbation theory (MPPT).

The accuracy of many-body method can be measured in terms of the perturbation order. Thus, MBPT is a very efficient tool for calibrated measurement of energy and wave function. The MP based RSPT is now commonly used for correlated calculations of atoms and molecules.

The disadvantage of perturbation theory is that, convergence is not guaranteed by the method.

I.6.E. Coupled cluster (CC) method:

The state-of-the-art method in electronic structure theory is coupled cluster (CC) method. Coupled cluster method was first introduced in nuclear physics by Coester, Coester and Kümmel [184]. The coupled cluster theory in electronic structure theory was developed from the pair correlation theory of Sinanoğlu [173] and Nesbet [174]. Hubbard [185] applied diagrammatic MBPT and showed that the exact ground state wave function of many-electron system can be written in an exponential form. Čížek and Paldus [163c] first introduced coupled cluster theory in electronic structure theory.

The dynamical electron correlation in CC wave function is brought in through an exponential wave-operator operating on the reference function; generally the HF wave function is considered as reference wave function. In coupled cluster theory the wave function is expressed as:

$$\left|\Psi_{cc}\right\rangle = e^{T}\left|\Phi_{0}\right\rangle \tag{I.41}$$

The exponential nature of operator, truncated CC functions introduce the unlinked higher body excitation terms.

Usually, intermediate normalization is applied for wave function. Here T is known as cluster operator. The cluster operators commute with each other T is neither hermitian nor anti hermitian. In terms of diagrammatic representation, T contains only the upward open connected wave function diagrams. The cluster operator can be written as sum of electron-excitation operators, *viz*, one-electron, two-electron, etc.

$$T = T_1 + T_2 + T_3 + ... + T_N \tag{I.42}$$

Where, the terms in the right hand side can be written in terms of second quantization as:

$$\begin{aligned} T_1 &= \sum_{i,a} t_i^a a_a^+ a_i \\ T_2 &= \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i \\ &. \\ &. \\ T_N &= \sum_{\substack{i>j>k.... \\ a>b>c....}} t_{ijk..}^{abc..} a_a^+ a_b^+ a_c^\dagger a_k a_j a_i \end{aligned} \tag{I.43}$$

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

Since in Equation (I.41) only one single determinant is taken as reference function, that’s why this method is known as single reference coupled cluster method (SRCC).

In the exact limit of full CC has correspondence with FCI. We can write

$$\begin{aligned} C_1 &= T_1 \\ C_2 &= T_2 + \frac{1}{2!}T_1^2 \\ C_3 &= T_3 + T_1T_2 + \frac{1}{3!}T_1^3 \\ C_4 &= T_4 + T_1T_3 + \frac{1}{2!}T_2^2 + \frac{1}{4!}T_1^4 \end{aligned} \tag{I.44}$$

The cluster amplitudes in CC method are treated as independent parameters. Substituting Equation (I.41) into Schrödinger equation with normal ordered Hamiltonian leads to:

$$H_N e^T \left|\Phi_0\right\rangle = \varepsilon_{corr} e^T \left|\Phi_0\right\rangle \tag{I.45}$$

If we project from left of Equation (I.45) by $\left|\Phi_0\right\rangle$ and various excited determinants ($\left|\Phi_{ij\ldots}^{ab\ldots}\right\rangle$) separately, we shall get equations, from where we can get the correlation energy and amplitudes.

$$\left\langle\Phi_0\right|H_N e^T\left|\Phi_0\right\rangle = \varepsilon_{corr}\left\langle\Phi_0\right|e^T\left|\Phi_0\right\rangle \tag{I.46}$$

Expanding the right hand side of Equation (I.46), we shall see due to normalization condition, only the term survive which does not contain T, others will become zero. Thus, the Equation (I.46) becomes:

$$\left\langle\Phi_0\right|H_N e^T\left|\Phi_0\right\rangle = \varepsilon_{corr} \tag{I.47}$$

$$\left\langle\Phi_{ij\ldots}^{ab\ldots}\right|H_N e^T\left|\Phi_0\right\rangle = \varepsilon_{corr}\left\langle\Phi_{ij\ldots}^{ab\ldots}\right|e^T\left|\Phi_0\right\rangle \tag{I.48}$$

From Equation (I.47) we get the correlation energy and the cluster amplitudes can be obtained from Equation (I.48).

The right side of Equation (I.48) is not a number, that’s why we have to consider unlinked, open diagrams also. Because of e^T term, the unlinked terms of both sides of Equation (I.48) get mutually canceled. Thus, Equation (I.47) and Equation (I.48) can be written as:

$$\varepsilon_{corr} = \left\langle\Phi_0\right|H_N e^T\left|\Phi_0\right\rangle_{closed,connected} \tag{I.49}$$

$$\left\langle\Phi_{ij\ldots}^{ab\ldots}\right|H_N e^T\left|\Phi_0\right\rangle_{open,linked} = 0 \tag{I.50}$$

Similarly, for single hole-particle excitation we can write:

$$\left\langle \Phi_i^a \middle| H_N e^T \middle| \Phi_0 \right\rangle_{open,connected} = 0$$

The disconnected terms of Equation (I.48) for double excitations can occur as product of connected single excitation terms $\left\langle \Phi_i^a \middle| H_N e^T \middle| \Phi_0 \right\rangle_{open,connected}$, with singly excited cluster amplitude $\left(t_j^b\right)$ disappears from final equations. In the same way, the connected, open terms survive in Equation (I.48), leading to completely connected CC equations

$$\varepsilon_{corr} = \left\langle \Phi_0 \middle| H_N e^T \middle| \Phi_0 \right\rangle_{closed,connected} \qquad \text{(I.49)}$$

$$\left\langle \Phi_{ij\ldots}^{ab\ldots} \middle| H_N e^T \middle| \Phi_0 \right\rangle_{open,connected} = 0 \qquad \text{(I.51)}$$

Because of commutation relation between the cluster operators, one cluster operator cannot contract with another cluster operator. This fact implies that when we attempt to draw CC diagrams, each cluster operator in the diagram should be connected with Hamiltonian vertex not with each other. On the other hand the Hamiltonian operator consists of two parts, *viz.*, one body (f) and two-body (V), that is why the Hamiltonian can have a maximum of four lines for such connections. Again by Slater rule [2], each term of Equation (I.51), can have a maximum of four cluster operators. Therefore the CC equations are algebraic non-linear equations in unknown cluster amplitudes and are at most of quatric power. On the other hand, from Equation (I.49), correlation energy contains only one-body and two-body cluster operators, which are coupled to higher-body cluster operators via Equation (I.51).

The above CC equations can be derived in another way [9, 84, 159] by pre-multiplying Equation (I.45) by e^{-T} and we get:

$$e^{-T}H_Ne^T\left|\Phi_0\right\rangle = \varepsilon_{corr}\left|\Phi_0\right\rangle \tag{I.52}$$

The non-hermitian operator, $\bar{H} = e^{-T}H_Ne^T$ nothing but the original Hamiltonian, H_N similarity transformed ($X^{-1}AX$) by an invertible operator, $X = e^T$. Thus, Equation (I.52) can be viewed as an eigen value equation for the similarity transformed Hamiltonian, $\bar{H}$. It is also known that the similarity transformation does not change its eigen values. Thus, to derive Equation (I.47) and Equation (I.48), we follow the same procedure and get the following set of equations:

$$\varepsilon_{corr} = \left\langle\Phi_0\right|e^{-T}H_Ne^{T}\left|\Phi_0\right\rangle \tag{I.53}$$

$$\left\langle\Phi_{ij....}^{ab....}\right|e^{-T}H_Ne^{T}\left|\Phi_0\right\rangle = 0 \tag{I.54}$$

If two operators A and B are having the form: $e^{-A}Be^{A}$, Campbell-Baker-Hausdroff (CBH) formula can be applied. According to CBH formula $e^{-A}Be^{A}$ can be expanded as:

$$\begin{gathered} e^{-A}Be^{A} = B + \left[B,A\right] + \frac{1}{2!}\left[\left[B,A\right],A\right] + \\ \frac{1}{3!}\left[\left[\left[B,A\right],A\right],A\right] + \frac{1}{4!}\left[\left[\left[\left[B,A\right],A\right],A\right],A\right] + ... \end{gathered} \tag{I.55}$$

Similarly, the similarity transformed Hamiltonian, $\bar{H} = e^{-T}H_Ne^{T}$ becomes:

$$\bar{H} = e^{-T} H_N e^{T} = H_N + \left[H_N, T\right] + \frac{1}{2!}\left[\left[H_N, T\right], T\right] + \frac{1}{3!}\left[\left[\left[H_N, T\right], T\right], T\right] + \frac{1}{4!}\left[\left[\left[\left[H_N, T\right], T\right], T\right], T\right] + . \qquad \text{(I.56)}$$

Due to the two body nature of H_N and commutative nature of cluster operator, this series can be shown to terminate after four fold commutation. The connected nature of correlation energy and cluster amplitudes are explicitly revealed by the presence of commutators Equation (I.56), with H_N being connected, its commutation with cluster operators, generates only connected terms, eventually leading to a completely connected series.

Equation (I.54) can be represented as condition to make the lower triangular block of H_N to vanish. This facilitates finding the corresponding eigen value of H_N, which in turn is equivalent to calculate ε_{corr}. Derivation of CC equations by applying BCH formula shows that CC method may be viewed as diagonalization of similarity transformed Hamiltonian to obtain correlation energy. This is also useful to understand various generalization of CC method for multi-reference as well as equation-of-motion CC (EOM-CC) methods for excited states [108, 159].

As we discussed earlier in FCI, it is impractical because of computation cost, that’s why we have to truncate upto a certain excitation. Since double excitations are dominant in the first-order MBPT wave-function based on closed-shell RHF vacuum $|\Phi_0\rangle$, in a same way we can say that the two-body cluster operator T_2 is expected to be most important. Čížek [163a] first approximated that truncating the cluster operator up to its two-body part, *i.e.*, $T \cong T_2$ and named as coupled-pair many-electron theory (CPMET). Now-a-days CPMET is known as coupled cluster doubles (CCD). The same name was given by Sinanoğlu [173b]. Sinanoğlu used a kind of stationary principle on dominant part of the energy functional. On the other hand, Čížek adopted a non-variational strategy involving solution of Equation (I.51) for determining the two-body cluster amplitudes.

Bartlett *et al*. [186] and Pople *et al*. [187] independently started systematic development and application of CC method. Bartlett *et al*. [186] had done by using spin-orbital form. On the other hand Pople *et. al*. [187] applied CC method, where the cluster operators are truncated to include one-body, two-body cluster operator, *i.e.*, $T \cong T_1 + T_2$ and is known as coupled cluster singles doubles (CCSD) method. Noga and Bartlett [188] truncated up to triples cluster inclusion, *i.e.*, $T \cong T_1 + T_2 + T_3$ and is referred to as coupled cluster singles doubles triples (CCSDT) method [189]. The CCSDT methods are particularly very important for molecules with high electron densities, multiple bonds, etc. The CCD, CCSD and CCSDT methods represent a hierarchy of increasing accurate CC methods. Kucharski and Bartlett [190] extended this hierarchy by including quadruple cluster operator, *i.e.*, $T \cong T_1 + T_2 + T_3 + T_4$ and is known as coupled cluster singles doubles triples quadruple (CCSDTQ) method. One thing to mention in this context is that we can never truncate the cluster operator only up to T_1, *i.e.*, $T \cong T_1$, *i.e.*, coupled cluster singles (CCS), because of Thouless theorem. [191].

Advantage of truncating up to double excitations is that, by CCD wavefunction we can include not only the double excitations, but also include higher body excitations, *e.g.* quadruple, hexapole. Exponential nature of the CC wavefunctions naturally includes such excitations, and hence may be considered to be a better representation as we compare with the CI counterpart. Another advantage of CC method is that the approximate CC methods are obtained by truncating the cluster operator, are also size-extensive as well as size-consistent. The amplitude equations are represented by only connected open diagrams. It can be shown that the cluster operators calculated from these equations are additively separable and can be represented by connected diagrams of the Hamiltonian with the cluster operator.

Since CC equations are represented by only connected open diagrams, it can be shown that the cluster operator calculated from these equations are additively separable. That’s why they can be represented by connected diagrams of Hamiltonian with cluster operator. The CC correlation energy is also additively separable and hence size extensive. Additive separability is ensured by exponential nature of the wave function. It also ensures size-consistency of CC method, subject to the condition that the reference function properly separates under dissociation [161].

To solve algebraic non-linear cluster amplitudes of CC equations, Jacobi iteration procedure is adopted. Single iteration involves evaluation of products of cluster amplitudes with the Hamiltonian. Efficient factorization of CC equations along with matrix multiplication based technique to evaluate such product is well defined. Computational scaling of CCD and CCSD method is approximately $N_o^2 * N_v^4$ floating point operations per iteration, where N_o and N_v correspond to the number of occupied and virtual orbitals, respectively [84d]. Scaling rapidly increases as higher-body cluster operators are added, *e.g.* the scaling of CCSDT and CCSDTQ are $N_o^3 * N_v^5$ and $N_o^4 * N_v^6$, respectively [84d].

Correlation energy for CCD:

$$\varepsilon_{corr} = \sum_{i,j,a,b} \frac{\left[2\langle ij|ab\rangle - \langle ij|ba\rangle\right]\langle ij|ab\rangle}{\left(\varepsilon_i + \varepsilon_j\right) - \left(\varepsilon_a + \varepsilon_b\right)}$$

This is exactly same as the correlation energy obtained from MP2 energy. The relation between CC and MBPT is well studied [98, 192]. For each iteration CC equations generate an additional set of MBPT diagrams for both energy and wave function. For this reason CC method can be viewed as a way to systematically sum selected classes of MBPT diagrams to infinite order. In other words, CC method is an indirect way to carry out a partial infinite-order summation of MBPT diagrams [84d]. This relation is useful for CCSD and CCSDT methods.

The CC method formulation is based on spin-orbitals. Thus, CC method is applicable to both closed and open shell molecules, described by single determinant, ROHF or UHF determinant. Such spin-orbital formulations are computationally demanding as they involve more number of cluster amplitudes than the minimum number dictated by spin-symmetry of the targeted state. Spin-integration is introduced to overcome the problem in spin-orbital CC formulations based on closed-shell RHF determinant, represented as $|vac\rangle$. Spin integration is usually performed by choosing an independent set of cluster amplitudes depending only on the spatial orbitals and associating certain spin-integration factors to the terms in CC equations. It is known that this procedure is equivalent to spin-adaptation of CC method, such excited state configuration obtained by the action of cluster operator on RHF determinant are non-orthogonal. Using graphical method of angular momentum for spin-adapting various cluster operator Paldus [98] have obtained an orthogonally spin-adapted CC formulations applicable for closed shell states based on closed shell RHF determinant.

I.6.E.i. Various SRCC approaches:

Although coupled cluster method is explicitly a non-variational method, but, there are several ways to solve Equation (I.45). Normal coupled cluster (NCC) or single reference coupled cluster (SRCC) method is neither variational, nor perturbative. Coupled cluster equation can also be casted in a variational framework. In this approach energy functional is written as an expectation value and amplitude equations are obtained using variation of the energy with respect to cluster amplitudes. Expectation value, unitary value coupled cluster (XCC, UCC) [193], extended coupled cluster [194-199]are few of the functions used in stationary or variational CC theory. Variational CC is more complex compared to SRCC. Being variational it has natural advantage in the calculation of energy derivatices.

I.6.E.i.1. Expectation value and unitary coupled-cluster (XCC and UCC) ansatz:

In variational CC approach energy function is made stationary with respect to cluster amplitudes. In expectation value theory we can write energy function as expectation value of Hamiltonian.

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

$$= \frac{\langle \Phi_0 | e^{T^\dagger} H e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle} \tag{I.57}$$

Here $T^\dagger$ is hole-particle destruction operator. The function is Hermitian but non-terminating. It is shown by Pal *et al.* [150] that the function can be written as:

$$E = \langle \Phi_0 | e^{T^\dagger} H e^T | \Phi_0 \rangle_{conn} \tag{I.58}$$

The above energy expression is a non-terminating series and needs to be truncated for practical application. Pal and co-workers [193] used truncation scheme based on the number of cluster amplitudes. Though energy functional is connected the equation for cluster amplitude contains disconnected diagrams Bartlett and co-workers [200] used linear truncation scheme based on perturbation order. The perturbative truncation scheme ensures size extensivity at each order. However, it misses out important terms of lower order. Whereas, some terms involving higher order cluster amplitudes would be included when truncation is based on number of T amplitudes, it leads to disconnected diagrams in cluster amplitude equations. The amplitude equations are obtained using following equation:

$$\frac{\partial E^{(0)}}{\partial t^{(0)}} = 0 \tag{I.59}$$

Van Vleck [201], Primas [202] and Kutzelnigg [177] proposed another approach in variational CC method. This approach is called unitary coupled cluster (UCC) method. In UCC, the functional is given by:

$$\left|\Psi_{ucc}\right\rangle = e^{\sigma}\left|\Phi_0\right\rangle \tag{I.60}$$

Here, σ is anti-hermitian. σ is chosen as $\sigma = T - T^{\dagger}$. $\sigma^{\dagger} = T^{\dagger} - T$ and $\sigma^{\dagger} = -\sigma$. Cluster amplitudes may be obtained by using variational or non-variational amplitudes. The non-variational [203] is closely resembles to NCC approach and the set of equations can be obtained by replacing the T in the NCC equations by σ.

Kutzelnigg [176] proposed that UCC can be solved variationally. The energy function in UCC functional can be written as:

$$\begin{aligned} E &= \frac{\left\langle \Phi_0 \middle| e^{-\sigma} H e^{\sigma} \middle| \Phi_0 \right\rangle}{\left\langle \Phi_0 \middle| e^{-\sigma} e^{\sigma} \middle| \Phi_0 \right\rangle} \\ &= \left\langle \Phi_0 \middle| e^{-\sigma} H e^{\sigma} \middle| \Phi_0 \right\rangle \end{aligned} \tag{I.61}$$

Thus, the UCC equation becomes similarity transformed like NCC, but the σ amplitudes are obtained variationally like XCC. Bartlett and Noga used UCC (n) [202] ansatz analogous to XCC (n). However, unlike XCC (n), UCC (n) functional is symmetric.

I.6.E.i.2. Extended coupled-cluster (ECC) ansatz:

Arponen [194a] by adding one more similarity transformation on the Hamiltonian using hole particle destruction operators derived the following expression.

$$E_0^{corr} = \left\langle \Phi_0 \middle| e^S e^{-\tau} H_N e^{\tau} e^{-S} \middle| \Phi_0 \right\rangle \qquad (I.62)$$

The above equation is known as extended coupled cluster (ECC) [194-199]. In Equation (I.62) τ is known as hole-particle creation operators and characteristically identical as T operators in NCC. On the other hand S operator is just the reverse of τ and are known as hole-particle destruction operator, and identical to τ operators used in XCC, but not conjugate with τ. After double similarity transformation the final form of ECC functional is:

$$E_0^{corr} = \left\langle \Phi_0 \middle| e^S [H_N e^{\tau}]_{linked} \middle| \Phi_0 \right\rangle_{Double\ \ linked} \qquad (I.63)$$

The first linking is contraction between τ and H. Double linking implies that the S operator, if not directly connected to the Hamiltonian, must contract with least two distinct τ operators. The double linking ensures the connectedness of the terms of the equations for S and τ, which are obtained by making the energy stationary with respect to t and s amplitudes separately. ECC gurantees size-extensivity and size consistency. Piecuch and Bartlett [203] proved that ECC is size-extensive.

I.7. Quasi-degeneracy:

The single reference (SR) methods can successfully describe those states, where single determinant, Φ_0 is dominating. Closed-shell atoms, near equilibrium ground state of molecules belong to this category. Although, some open-shell states can be described by using a dominant UHF or ROHF based SR methods. SR methods are suitable to describe dynamic correlation [92a], but in chemistry, some situations arise, where various determinants contribute equally in accurate description of a state [92a, 109]. This is known as quasi-degeneracy. In open-shell atoms, excited, electron attached or detached states of atoms and molecules, reaction transition states, bond-dissociation processes this phenomenon is observed. A quasi-degenerate state is characterized by a significant amount of non-dynamical electron correlation. Non-dynamical correlation arises due to interaction between dominant determinants.

I.8. Single-reference based methods to treat non-dynamical correlation:

In general to handle quasi-degeneracy multi-reference based methods are used. However, there are some methods which can take care of quasi-degenerate problem within SR frame work. Symmetry adapted cluster configuration interaction (SAC-CI) [129, 130], equation-of-motion coupled cluster (EOM-CC) [122-126], reduced multi-reference coupled cluster (RMRCC) method [204, 205], active-space coupled cluster approach [206], tailored CCSD [207], orbital-optimized coupled cluster scheme [208], spin-flip methods [209], higher-order non-iterative corrections derived from similarity-transformed Hamiltonian [210], renormalized coupled cluster methods [211], etc are belong to this category. These methods can handle quasi-degeneracy. Among these the first two methods are briefly described in the next two sub-sections.

I.8.A. Symmetry adapted cluster configuration interaction (SAC-CI):

For a singlet closed shell state symmetry adopted cluster (SAC) wave function is:

$$\begin{aligned}\Psi_{ground}^{SAC} &= \exp\left(\sum_i \left(C_i S_i\right)\right)\left|\Phi_0\right\rangle \\ &= \left(1+\sum_i C_i S_i + \frac{1}{2}\sum_i C_i C_j S_i S_j + ...\right)\left|\Phi_0\right\rangle\end{aligned} \tag{I.64}$$

S_i is symmetry adapted excitation operator.

$$\left\langle \Phi_0 \middle| \left(H - E_{ground}\right) \middle| \Psi_{ground}^{SAC} \right\rangle = 0 \tag{I.65}$$

$$\left\langle \Phi_0 \middle| S_i \left(H - E_{ground}\right) S_i^{\dagger} \middle| \Psi_{ground}^{SAC} \right\rangle = 0 \tag{I.66}$$

This is non-variational way of solving SAC equations. In a variational approach equations are:

$$\left\langle \Psi_{ground}^{SAC} \middle| \left(H - E_{ground}\right) \middle| \Psi_{ground}^{SAC} \right\rangle = 0 \tag{I.67}$$

$$\left\langle \Psi_{ground}^{SAC} \middle| S_i \left(H - E_{ground}\right) S_i^{\dagger} \middle| \Psi_{ground}^{SAC} \right\rangle = 0 \tag{I.68}$$

Using variational or non-variational formulation equations can be obtained.

The excited function Φ_k are obtained using SAC wave function as:

$$\Phi_k = PS_k^\dagger \left| \Psi_{ground}^{SAC} \right\rangle \tag{I.69}$$

$$P = 1 - \left| \Psi_{ground}^{SAC} \right\rangle \left\langle \Psi_{ground}^{SAC} \right| \tag{I.70}$$

P is an operator that projects out SAC function:

$$\left\langle \Phi_k \middle| \Psi_{ground}^{SAC} \right\rangle = 0 \tag{I.71}$$

$$\left\langle \Phi_k \middle| H \middle| \Psi_{ground}^{SAC} \right\rangle = 0 \tag{I.72}$$

SAC-CI can also be used for electron attached or detached states. The general form of the Φ_k wave function can be written as:

$$\Phi_k = PR_k^\dagger \left| \Psi_{ground}^{SAC} \right\rangle \tag{I.73}$$

Where, R_k's are excitation, electron attach/detachment operator.

I.8.B. Equation-of-motion coupled cluster (EOM-CC) method:

The equation of motion (EOM) formulation is one of the tools used in quantum chemistry to obtain direct difference energies. In EOM-CC approximation the exact electronic wave function can be written as:

$$\left| \Psi_{EOM-CC} \right\rangle = R \left| \Psi_{cc} \right\rangle \tag{I.74}$$

Where, $\left| \Psi_{cc} \right\rangle$ is defined in Equation (I.41). R_1 is defined as:

$$R = r_0 + \sum_{ia} r_i^a \left\{ a^\dagger i \right\} + \sum_{\substack{a,b \\ i,j}} r_{ij}^{ab} \left\{ a^\dagger i b^\dagger j \right\} \tag{I.75}$$

Where, R and T are excitation operators and $\left|\Phi_0\right\rangle$ is the HF wave function. R_1 and T commute with each other. Substituting the above wave function in Schrödinger equation we get:

$$H\,\mathrm{Re}^{T}\left|\Phi_0\right\rangle = E\,\mathrm{Re}^{T}\left|\Phi_0\right\rangle \tag{I.76}$$

Premultiplying by e^{-T} we get:

$$e^{-T}He^{T}R\left|\Phi_0\right\rangle = E\,\mathrm{Re}^{-T}\mathrm{e}^{T}\left|\Phi_0\right\rangle \tag{I.77}$$

$$\bar{H}R\left|\Phi_0\right\rangle = ER\left|\Phi_0\right\rangle \tag{I.78}$$

$\bar{H}$ is non-Hermitian and has left and right eigen vectors:

$$\begin{aligned} L\bar{H} &= EL \\ \bar{H}R &= ER \end{aligned} \tag{I.79}$$

Left and right vectors can be normalized so that they are biorthogonal:

$$L_i R_j = \delta_{ij} \tag{I.80}$$

I.9. Multi-reference based methods:

To treat non-dynamical correlation properly, we have to first specify the zeroth-order reference state, $\Psi^{(0)}$ as an approximation to the desired quasi-degenerate state Ψ. $\Psi^{(0)}$ is generally constructed as a linear combination of a set of M strongly interacting determinants ($\Phi_I, I = 1,2,..,M$). $\Psi^{(0)}$ can be obtained in many ways. For a given state, $\Psi^{(0)}$ is not unique. Non-dynamic correlation is calculated by using an appropriate multi-reference method, and brings a correction terms X for the wave-function.

$$\Psi^{(0)} = \sum_{I=1}^{M} C_I \Phi_I$$

$$\Psi = \Psi^{(0)} + X \tag{I.81}$$

By introducing multi-reference (MR) [109] method, non-dynamic correlation can be treated by employing multi-determinantal zeroth-order description.

The set of strongly interacting determinants (Φ_I) contributes to zeroth-order description of a given quasi-degenerate state and is usually found to be adequate to construct zeroth-order description of some of quasi-degenerate states. The space spanned by (Φ_I) contains the zeroth-order reference states of a manifold of quasi-degenerate states and is known as model or reference space, denoted by P. The space spanned by all determinants which not belonging to the model space are referred as complement space (Q). The model space is considered as zeroth order approximation to the space P of some exact quasi-degenerate states of the full Hamiltonian H, with their reference states in P.

To choose model space, we shall first define three important terms:

(1) The orbitals occupied in all the model space determinants are referred to as core or hole orbitals.

(2) The unoccupied orbitals in the model space determinants are referred to as particle, or, virtual orbitals.

(3) The orbitals which are occupied in only some of the model space determinants are referred to as active or valance orbitals.

Model space determinants differ in occupancies of only valance orbitals. To construct model space, we have to include some of the quasi-degenerate determinants. When all possible determinants are included in the model space, then it is called complete model space (CMS). On the other hand, in incomplete model space (IMS) all possible are not included in the model space.

We will discuss previously discussed methods within multi-reference frame-work:

A) Multi-configuration self consistent field method (MCSCF).

B) Multi reference configuration interaction method (MRCI).

C) Multi reference perturbation method (MRMP).

D) Multi reference coupled cluster method (MRCC).

I.9.A. Multi-configuration self consistent field (MCSCF) method:

In this section we will discuss the methods previously discussed in the context of single reference. However, now the reference space is multi-determinant.

Multi-configuration self consistent field (MCSCF) is another method which is very similar to CI method [2, 212, 213]. An MCSCF wave-function is a truncated CI expansion, where only a small number of selected determinants are important to describe a state are retained. In contrast to CI, both the expansion coefficient and orbitals are optimized to minimize the energy of MCSCF wave-function. This leads to equations somewhat similar in structure to the HF equations and are solved by a SCF approach. Complete active space MCSCF (CAS-SCF) is a variant of MCSCF and is used frequently [214]. In CAS-SCF, the determinants selected, to be included in the expansion are done by identifying a set of orbitals, known as active or valance orbitals. All the determinants are generated by distributing the given number of valance electrons, amongst all active orbitals included in the MCSCF expansion. Based on generalization of valance-bond approach of Heitler and London [215], there are several other various MCSCF method.

MCSCF wave functions can be used as reference states for multi-reference configuration interaction (MRCI), multi-reference perturbation theories, like complete active space second order perturbation theory (CASPT2), and can be dealt with various complex problems in quantum chemistry.

I.9.B. Multi-reference configuration interaction (MRCI) method:

The multi-reference configuration interaction (MRCI) [92a, 216-219] is a popular and standard method in quantum chemistry. In MRCI method, the wave function is constructed as linear combinations of all distinct excited determinants, generated by excitations on each determinant within the model space. MRCISD includes all single and double excitations, but thr difference is that here we have to do with respect to every determinant in the model space [92a].

$$\Psi_{MR-CISD} = \sum_{I=1}^{M} C_I \Phi_I + \sum_{S} C_S \Phi_S + \sum_{D} C_D \Phi_D \qquad \text{(I.82)}$$

Φ_S and Φ_D are the singly and doubly excited determinants obtained from the set of reference functions (Φ_I), respectively. Generally, the model space contains singly and doubly excited determinants and the final MRCI wave function includes some triple and quadruple excitations. The coefficients 'C's are determined variationally leading to diagonalizing the Hamiltonian matrix evaluated between different determinants.

Presently MRCI methods use spin-adapted configuration state functions (CSF) instead of determinants, along with the efficient rules developed for evaluation of coupling coefficients entering in the Hamiltonian matrix elements. Excitations from each of the model space CSFs are considered. Total number of CSFs included in MRCI wave function, scales linearly with size of the model space. Applying MRCI is difficult in case of large model space, specifically large incomplete model space. If we compare with SRCI, the first-order interacting space of the reference determinant Φ_0 is spanned by all singly and doubly excited CSFs, but in MRCI the excited CSFs are included in MRCI expansion span a much bigger space than the first order interacting space of the zeroth order reference function. Instead of generating singly and doubly excited CSFs from each of the model space CSFs, configurations may be constructed by applying excitation operators to the contracted zeroth order reference function as a whole, and known as internally contracted configurations (ICC) [92a]. Meyer [220] showed that the set of excited ICCs of a zeroth order reference function span its first order interacting space. Werner and Reinsch [221] applied ICCs in MRCI, resulting in internally contracted MRCI (ICMRCI) method. Knowles and Werner [222] formulated the same in an efficient manner. Use of larger model spaces as compared to conventional model space is allowed in ICMRCI method. The ICCs are not orthogonal and depend on the combining coefficients of model space CSFs, that's why complication arises in evaluating the coupling constants and Hamiltonian matrix elements. To overcome this, recent approaches to ICMRCI includes a balanced combination of contracted CSFs [222].

Like truncated SRCI methods, truncated MRCI methods are also not size-extensive.

I.9.C. Multi-reference perturbation theory:

The multi-reference perturbation theory can be classified into two sub-classes [223]:

i) Multi-reference perturbation theory.

ii) Quasi-degenerate perturbation theory.

We shall discuss here both the theories. Before discussing the Quasi-degenerate perturbation theory, we shall briefly discuss the effective Hamiltonian formalism.

I.9.C.i. Multi-reference perturbation theory (MRPT):

The multi-reference perturbation theory (MRPT) follows the same formalism of single reference perturbation theory [93 a, b] but instead of single determinant multiple determinants are used.

In MRPT, a zeroth order wave function $\Psi^{(0)}$ describes the desired state. Construction of Ψ is done (mostly by MCSCF calculation) by diagonalizing the Hamiltonian over the model space. Ψ is then used to construct the zeroth order Hamiltonian $\left(H_0\right)$. The eigen functions, eigen values and perturbation are $\Psi^{(0)}$, E_0 and V, respectively. If perturbation is small, then the perturbation expansion around zeroth order wave function is used to calculate perturbative corrections to energies $\varepsilon^{(n)}$ and wave functions $\mathrm{X}^{(n)}$ for the desired states are:

$$\begin{aligned}
&H_0\Psi^{(0)} = E_0\Psi^{(0)} \\
&V = H - H_0 \\
&\Psi = \Psi^{(0)} + \mathrm{X} \qquad\qquad (\mathrm{I}.83) \\
&\mathrm{X} = \mathrm{X}^{(1)} + \mathrm{X}^{(2)} + \ldots. \\
&\varepsilon = E_0 + \varepsilon^{(1)} + \varepsilon^{(2)} + \ldots.
\end{aligned}$$

Using this approach, we can get one state at a time, *i.e.*, state specific [183] and is known as diagonalize-then-perturb approach.

When we calculate the zeroth order wave function, then maximum part of non-dynamical correlation energy is recovered. The unrecovered part is the state-specific dynamic correlation it is recovered in low orders of perturbation expansion around the zeroth order state. Thus, to recover the state-specific dynamic correlation, we have to adopt MRPT. MRPT is generally used to calculate the first order wave-function correction, $X^{(1)}$. MRPT is sufficient to calculate up to third order.

A special case of MRPT is complete active space second order perturbation theory (CASPT2). In this method, second order MRPT approach is applied using CASSCF wave function as zeroth order wave function. This method is developed by Roos *et al*, [224]. In CASPT2, the second order wave function is expanded in terms of excited ICCs. Wolinski *et al.* [225], Dyall [226] and Celani *et al.* [227] adopted similar approach for MRPT development. Instead of ICCs, uncontracted CSFs can be used to expand the first order wave function. This method leads to another variety of MRPT, developed by Murphy and Messmer [228], Hirao [229] Kozlowski and Davison [230].

Choice of zeroth order Hamiltonian is the most difficult part in MRPT. Generally, in multi-reference problems, the zeroth order Hamiltonian is non-diagonal, that's why a set of linear equations have to solve to determine the first order wave function.

I.9.C.ii. Effective Hamiltonian approach:

Using effective Hamiltonian approach an alternative way of developing multi reference based theories. In this approach a simultaneous description of a manifold of quasi-degenerate states can be attempted [95, 108, 231]. The concept of effective Hamiltonian is based on the partitioning N-electron Hilbert space into a smaller M-dimensional model space P and its complimentary Q

space. The model space consists of a set of M determinants ($\Phi_I, I = 1,....,M$), and Q is constructed over the rest ($\Phi_J, J = M+1,....,\infty$), and $P+Q=1$. The model space is approximated as M-dimensional target space P spanned over a set of M quasi-degenerate exact states; $\{\Psi_A, A=1,....,M\}$ of the full Hamiltonian H with corresponding energies ($E_A, A=1,....,M$), implying that each quasi-degenerate state in P has a significant component in the model space [99].

If the eigen values of a Hamiltonian are identical to the energies of quasi degenerate states of the Hamiltonian, belong to the target space P, then this Hamiltonian is called effective Hamiltonian, and is denoted by H_{eff}. The corresponding eigen vectors ($\Psi_A^{(0)}, A=1,....M$) of the H_{eff} within the model space represent an approximation to the corresponding quasi-degenerate states ($\Psi_A, A=1,....,M$) of H:

$$H_{eff}\Psi_A^{(0)} = \varepsilon_A \Psi_A^{(0)} \quad \forall A = 1,....,M$$

$$\Psi_A^{(0)} = \sum_I C_{IA}\Phi_I \tag{I.84}$$

$$\Psi_A = \Psi_A^{(0)} + \mathrm{X}_A$$

In the model space the H_{eff} effectively plays the role of the full Hamiltonian H and that's why the name 'effective Hamiltonian' [108, 231, 232]. The H_{eff} is defined over entire Hilbert space, but usually it is constructed such that only its matrix elements over the model space are required for the purpose of its diagonalization to obtain ε_A and $\Psi_A^{(0)}$ It proceeds via defining valence universal operator, known as wave operator, Ω, which relates the eigen vectors of H_{eff} to the corresponding exact quasi-degenerate states of H.

$$\Omega\Psi_A^{(0)} = \Psi_A \quad \forall A$$

$$\Psi_A = \Omega\Psi_A^{(0)} \tag{I.85}$$

$$P = \Omega P$$

Kato [233], Bloch [234], and des Cloizeaux [235] introduced the concept of effective Hamiltonian. The effective Hamiltonian can be constructed by following two ways:

I.9.C.ii.1. Similarity transformation approach:

In this method a similarity transformation of H is carried out, by the wave operator, Ω to obtain an operator $\bar{H}$:

$$\bar{H} = \Omega^{-1}H\Omega \tag{I.86}$$

Similarity transformation ensures that all eigen values of $\bar{H}$ are same as those of H. This implying that $\bar{H}$ can be used as H_{eff}. If the eigen vectors of $\bar{H}$ corresponding to the quasi-degenerate staes in P lies entirely within model space. The wave operator is determined in such a way that $\bar{H}$ becomes diagonal with respect to model space and essentially developed eigen value equation of $\bar{H}$, corresponding to the quasi-degenerate states in P from the eigen value equations for other states [232]. To define $\bar{H}$, we generally employ the minimal decoupling scheme, leading to a block triangular form for H_{eff}.

$$
\begin{aligned}
&Q\bar{H}P = 0 \\
&H_{eff} = P\bar{H}P + Q\bar{H}Q + P\bar{H}Q
\end{aligned}
\tag{I.87}
$$

In this approach, the H_{eff} is assumed to be an operator within the entire Hilbert space [232], but only its model space component $P\bar{H}P$ is relevant to obtain the eigen values and eigen vectors of desired quasi-degenerate states. This approach requires that Ω^{-1} exsits.

I.9.C.ii.2. Bloch equation approach:

In Bloch equation approach, the Schrödinger equation for all the quasi-degenerate states in P is expressed as:

$$
\begin{aligned}
&H\Omega P = \Omega H_{eff} P \\
&H_{eff}^{Bloch} = PH\Omega P \\
&QH\Omega P = Q\Omega PH\Omega P
\end{aligned}
\tag{I.88}
$$

Equation (I.88) is known as Bloch equation [83, 100, 109, 234]. In this formalism, the matrix elements of H_{eff} over only the model space enter into the Bloch equation.

For both these approaches, a normalization condition fixes its matrix elements over the model space, *i.e.*, $P\Omega P$. Usually specified through parameterization of Ω. Intermediate normalization scheme, *i.e.*, $P\Omega P = P$ [100] is the most commonly used method. Intermediate normalization implies that the projection of exact quasi-degenerate state in P onto P is nothing but the corresponding eigen functions of H_{eff}, within the model space.

Alternatively, we can say, if intermediate normalization is applied, then, no additional component lying within the model space will be generated by action of Ω on the model space.

The differences between the above two approaches are:

1) Similarity transformation based approach can be applied only when Ω^{-1} is available, and we can evaluate the operator $\Omega^{-1}H\Omega$. H_{eff} can be defined in terms of Ω. On the other hand in the Bloch equation approach explicit form of Ω^{-1} is not required, and H_{eff} is in general not an explicit function of Ω. Thus, to solve for H_{eff} we have to adopt iterative method along with Ω [100, 232]. H_{eff} can be defined in terms of Ω, only when intermediate normalization is used.

2) In the first case the matrix elements of H_{eff} over the entire Hilbert space are available, computationally easier and can be used for other purposes. On the other hand, second method involves the matrix elements of H_{eff}, only within the model space [232].

Varieties of effective Hamiltonians with different properties are there in literature [108, 231], Bloch's [234] approach is simplest among them.

The Bloch's effective Hamiltonian is non-hermitian [108, 231]. Des Clozieaus [235] derived a hermitian effective Hamiltonian by transforming the right eigen vectors of Bloch's effective Hamiltonian into an orthogonal set. For further studies on effective Hamiltonian see ref. [108, 231].

In the effective Hamiltonian formalism, both perturbative as well as non-perturbative scheme to compute Ω and H_{eff} can be formulated. Perturbative schemes lead to quasi-degenerate perturbation theory, and the non-perturbative counterpart leads to multi-reference coupled cluster methods.

Kirtman [236], Malrieu *et al*, [233, 237] proposed intermediate Hamiltonian approach, which is similar to effective Hamiltonian scheme.

In the intermediate Hamiltonian approach the intermediate Hamiltonian provides exact energy of a subset of quasi-degenerate states (*cf.* effective Hamiltonian provides exact energies of all the quasi degenerate states associated with M-dimensional model space). This approach is useful and flexible to avoid certain convergence problems associated with constructing the effective Hamiltonians, where, some of the targeted quasi-degenerate states do not have significant component within the model space. Mukherjee *et al*. [238] and Meissner *et al*. [232, 239] applied the intermediate Hamiltonian approach to formulate non-perturbative coupled-cluster scheme.

I.9.C.iii. Quasi-degenerate perturbation theory (QDPT):

In quasi-degenerate perturbation theory (QDPT), the perturbation expansion is carried out over entire quasi-degenerate target space P around the model space P [81, 95] (*cf.* in MRPT expansion is carried out over a single quasi-degenerate state around a zeroth order model space). As discussed in section I.6.D, that in the single-reference perturbation theory, the Hamiltonian is separated into two parts, *viz*. the zeroth order Hamiltonian, H_0 and a small perturbation term, V. H_0 is constructed in such a manner that the model space, P and its complementary space Q are its eigen subspaces. Assuming P and Q are well separated with respected to H_0 in terms of energy. Usually H_0 is constructed is such a manner that determinants in P and Q are eigen functions of H_0 [81, 95], and model space provides a zeroth order approximation for the target space. In such circumstances, the complementary space interacts weakly with the model space through V and perturbation is well-defined.

In the effective-Hamiltonian formalism, perturbation expansion is carried out for wave-operator Ω, and effective Hamiltonian, H_{eff} can be expressed as:

$$\begin{aligned} &\Omega = \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} + ... \\ &H_{eff} = H_0 + H_{eff}^{(1)} + H_{eff}^{(2)} + ... \end{aligned} \tag{I.89}$$

Based on Ω and H_{eff}, different types of QDPT can be formulated, *e.g.*, $H = H_0 + V$, for Bloch’s effective Hamiltonian in Equation (I.88), leads to generalized Bloch equation [81, 95]. Expression for degenerate model space is:

$$[\Omega, H_0]P = V\Omega P - \Omega PV\Omega P \tag{I.90}$$

$$H_{eff}^{Bloch} = PH_0P + PV\Omega P \tag{I.91}$$

Substituting Ω from Equation (I.89) in Equation (I.90), leads to expression for $\Omega(n)$ in terms of lower order quantities [81, 95].

$$\begin{aligned} &\left[\Omega^{(n)}, H_0\right]P = V\Omega^{(n-1)}P - \sum_{m=1}^{n-1}\Omega^{(n-m)}PV\Omega^{(m-1)}P \\ &\Omega^{(0)} = 1 \end{aligned} \tag{I.92}$$

Equation (I.92) is used to generate order-by-order many-body Rayleigh-Schrödinger (RS) perturbative equation to determine Bloch's effective Hamiltonian and wave-operator. For a complete degenerate model space, Brandow [240] proved that unlinked diagrams are present in any order of RS expressions for wave-operator and effective Hamiltonian gets canceled by each other.

QDPT has various forms, and are characterized by different requirements on the diagonal part of Ω. Because of the presence of intruder state convergence problem may come, while using complete model space [241]. Intruder states are functions formed from the complement space, having energies within the energy range of target states that leads to divergence in perturbation expansion. To overcome the convergence problem, such functions can be moved into the complementary space, and generally these model spaces are categorized as incomplete model space. Hose and Kaldor [242] applied incomplete model space (IMS) for the first time in QDPT.

I.9.D. Multi-reference coupled cluster theory (MRCC):

The MRCC theories are developed by getting exponentially parameterized ansatz for the wave operator and schemes are formulated to determine the parameters unambiguously by giving a platform for MRCC formalism to function within an effective Hamiltonian framework. The exponential parameterization is borrowed from SRCC theory, which maintains size-extensivity as well as size-consistency and gives highly accurate results.

This stems from partial infinite-order summation nature of CC theory. If we compare with SRCC, there is only one way to parameterize, but several parameterization schemes are available in MRCC theory [98, 100].

Within CMS it is easier to exponentially parameterize wave operator (Ω) to satisfy both intermediate normalization and size-extensivity. There are several classes of ansatz have been used, *viz*, state-universal (SU) or Hilbert space (HS) ansatz [118], valence-universal (VU) or Fock space (FS) ansatz [99, 109, 110, 119, 120], state-specific (SS) ansatz [101-106, 243], generalized multi-reference Brillouin–Wigner coupled cluster theory [244, 245]. In the next sub-sections we shall discuss a little-bit about these methods.

I.9.D.i. State-universal or Hilbert space multi-reference coupled cluster theory (SUMRCC/HSMRCC):

The state-universal multi-reference coupled cluster theory (SUMRCC) or Hilbert space multi-reference coupled cluster theory (HSMRCC) is proposed by Jezioroski and Monkhorst (JM) [118] and is useful in studying the potential energy surface of molecules [107a, 246]. In this formalism, a cluster operator is introduced for each model space determinant, and expression of the wave operator is:

$$\Omega = \sum_{\mu} e^{T_\mu} \left|\Phi_\mu\right\rangle\left\langle\Phi_\mu\right| \tag{I.93}$$

T_μ is the cluster operator, associated with the model space determinant. The structure of T_μ is similar to T in the SRCC. T_μ contains all hole-particle excitations. T_μ is chosen in such a way that T_μ operators cannot produce excitations within the model space. In the second quantized notation, Φ_μ is considered as hole-particle vacuum. The cluster amplitudes in T_μ, corresponding to the excitations leading to states within model space are set to zero, to satisfy the intermediate normalization [118]. The inverse of wave operator $\left(\Omega^{-1}\right)$ does not exist within the Hilbert-space containing same number of electrons as the model space determinants [118]. For this reason similarity transformation approach is not possible. Thus, to derive the standard forms of state-universal MRCC theory, we have to adopt Bloch's equation approach.

Using Bloch equation approach, the expression of the Hamiltonian becomes:

$$He^{T_\mu}\left|\Phi\right\rangle = \sum_{\nu} e^{T_\mu} H_{eff}^{\nu\mu} \qquad \forall\mu \tag{I.94}$$

The above equation can be solved in two ways,

1) Solution by using CBH formula.

2) Solution by avoiding CBH formula.

The two methods are discussed briefly:

I.9.D.i.1. Solution by using CBH formula:

Jezioroski and Monkhorst approach to solve Equation (I.94) is similar to the SRCC equations. Pre-multiplying Equation (I.94) by e^{-T_μ} and then left projection by Q and P (separately) leads to:

$$\left\langle \Phi_{\mu}^{*} \middle| e^{-T_{\mu}} H e^{T_{\mu}} \middle| \Phi_{\mu} \right\rangle = \sum_{\nu \neq \mu} \left\langle \Phi_{\mu}^{*} \middle| e^{-T_{\mu}} e^{T_{\nu}} \middle| \Phi_{\nu} \right\rangle H_{eff}^{\nu\mu} \quad \forall \mu \tag{I.95}$$

$$H_{eff}^{\nu\mu} = \left\langle \Phi_{\nu} \middle| e^{-T_{\mu}} H e^{T_{\mu}} \middle| \Phi_{\mu} \right\rangle \qquad \forall \mu, \nu \tag{I.96}$$

$$H_{eff} C = CE \tag{I.97}$$

$$\tilde{C} H_{eff} = \tilde{C} E \tag{I.98}$$

$$\tilde{C} H_{eff} C = E \tag{I.99}$$

$$\tilde{C} C = C \tilde{C} = 1 \tag{I.100}$$

Φ_{μ}^{*}s are the determinants in the Q-space, and consists of hole-particle excitation out of Φ_{μ}. From Equation (I.95), cluster amplitudes, T_{μ} can be calculated. Equation (I.96) describes the Bloch's effective Hamiltonian, $H_{eff}^{\nu\mu}$. Equation (I.97) and Equation (I.98) are defined to diagonalize $H_{eff}^{\nu\mu}$, resulting the right and left side, C and $\tilde{C}$, respectively. Equation (I.99) is used to calculate energy, which comes as a diagonal matrix of order $\mathrm{M} \times \mathrm{M}$, where M is the number of quasi-degenerate states under consideration, and the last equation, *i.e*. Equation (I.100) represents bi-orthonormal relation between C and $\tilde{C}$. Equation (I.95) is similar to SRCC equations. Left hand side is same as SRCC cluster amplitude equations and known as direct term. In SRCC, this part is explicitly connected. The terms on right hand side couple the cluster amplitudes of different vacuums are referred as renormalization terms. Using CBH formula for $e^{-T_{\mu}} e^{T_{\nu}}$, Jezioroski and Monkhorst did a perturbative proof of connectivity of cluster amplitudes and effective Hamiltonian. Renormalization term generates all folded diagrams of Brandow's open shell MBPT [240]. The quantities ($H_{eff}^{\nu\mu}, \forall = 1,....,M$) are evaluated by using normal-ordered expressions for H, with respect to determinant Φ_{μ} as vacuum:

$$H = H_0(\mu) + H_{0N}(\mu) + F_N(\mu) + V \qquad \text{(I.101)}$$

$H_0(\mu)$ is expectation value of H with respect to Φ_{μ} and N stands for normal-ordering. $H_{0N}(\mu)$ is a diagonal one-body operator containing orbital energies. $F_N(\mu)$, V are one and two body operator respectively. Elements of $F_N(\mu)$, depends on the orbitals obtained and reference vacuum [246]. V contains two-electron repulsion terms also.

Jezioroski and Monkhorst presented the truncation scheme for cluster operators for practical purpose. The renormalization term, arises because of CBH formula for $e^{-T_{\mu}}e^{T_{\nu}}$ are very complicated and generates a huge number of diagrams for further truncation. While deriving the spin-adapted version of SUMRCC theory with singles and doubles approximation (SUMRCCSD), Jezioroski *et al*. [247] derived systematically different truncations for direct as well as renormalization terms also. In this method size-consistency property is conserved at truncated levels, but the nature of resultant renormalization term becomes very cumbersome.

I.9.D.i.2. Solution by avoiding CBH formula:

To avoid CBH formula, Meissner, Kucharski, Balková, Bartlett [246, 248] proposed another method. Where, Q and P are projected from left of Equation (I.94), and generates:

$$\left\langle \Phi_{\mu}^{*} \middle| He^{T} \middle| \Phi_{\mu} \right\rangle = \sum_{\nu} \left\langle \Phi_{\mu}^{*} \middle| e^{T_{\nu}} \middle| \Phi_{\nu} \right\rangle H_{eff}^{\nu\mu} \quad \forall \mu \qquad \text{(I.102)}$$

$$H_{eff}^{\nu\mu} = \left\langle \Phi_{\nu} \middle| He^{T_{\mu}} \middle| \Phi_{\mu} \right\rangle \qquad \forall \mu, \nu \qquad \text{(I.103)}$$

If CBH formula is not applied, the (I.97), and (I.98) contain unlinked and disconnected terms and the unlinked terms get nullified and leads to size-extensive quantities [246]. Kucharski *et al.*, [246] derived the SUMRCCSD equations by diagrammatic representation, and model spaces with up to six-fold excitations.

I.9.D.ii. Valence-universal or Fock space multi-reference coupled cluster theory (VUMRCC/FSMRCC):

The valence-universal or Fock-space multi-reference coupled cluster theory (VUMRCC/FSMRCC) [99, 109, 110, 120, 121] is based on the concept of common vacuum. An N-electron RHF configuration is chosen as vacuum, with reference to this vacuum holes and particles are defined. These are further divided into active and inactive holes and particles. The model space determinant containing h-active hole and p-active particle is denoted as: $\Phi_{i}^{(p,h)}$. The model space of a $(p,\ h)$ valence Fock-space can be expressed as:

$$\Psi_{\mu}^{(0)(p,h)} = \sum_{i} C_{\mu i}^{(p,h)} \left| \Phi_{i}^{(p,h)} \right\rangle \qquad \text{(I.104)}$$

The exact wave function is written as:

$$\left| \Psi_{\mu}^{(p,h)} \right\rangle = \Omega \sum_{i} C_{\mu i}^{(p,h)} \left| \Phi_{i}^{(p,h)} \right\rangle \qquad \text{(I.105)}$$

Projection operator for the model space is:

$$P^{(p,h)} = \sum_i \left|\Phi_i^{(p,h)}\right\rangle\left\langle\Phi_i^{(p,h)}\right| \qquad \text{(I.106)}$$

Orthogonal component of the model space is:

$$Q = 1 - P \qquad \text{(I.107)}$$

Dynamic correlation is introduced via wave operator (Ω). Ω is defined in such a way that the states are generated by its action on the reference function must satisfy Schrödinger equation to generate the exact states for the $(p,\ h)$ valence system. Ω generates all probable excitation from the model space, and should contain cluster operators, $\tilde{T}^{(p,h)}$ and defined as:

$$\tilde{T}^{(p,h)} = \sum_{k=0}^{p}\sum_{l=0}^{h} T^{(k,l)} \qquad \text{(I.108)}$$

$T^{(k,l)}$ implies that the cluster operators are capable to create or destroy k-active particles and l-active holes. $\tilde{T}^{(p,h)}$ contains all lower $T^{(k,l)}$. Ω can be defined as:

$$\Omega = \left\{\tilde{T}^{(p,h)}\right\} \qquad \text{(I.109)}$$

The cluster operator in Equation (I.109) is normal ordered. The Schrödinger equation for the manifold of quasi-degenerate states can be written as:

$$H\left|\Psi_\mu^{(p,h)}\right\rangle = E_\mu\left|\Psi_\mu^{(p,h)}\right\rangle \qquad \text{(I.110)}$$

Using Equation (I.104) and left projecting Ω of both side of Equation (I.110) we have:

$$H\Omega\left(\sum_i C_{\mu i}^{(p,h)}\left|\Phi_i^{(p,h)}\right\rangle\right) = E_\mu\Omega\left(\sum_i C_{\mu i}^{(p,h)}\left|\Phi_i^{(p,h)}\right\rangle\right) \qquad \text{(I.111)}$$

Effective Hamiltonian for $(p,\ h)$ valence system can be defined as:

$$\sum_j \left(H_{eff}^{(p,h)} \right)_{ij} C_{j\mu} = E_\mu C_{i\mu} \tag{I.112}$$

$$\left(H_{eff}^{(p,h)} \right)_{ij} = \left\langle \Phi_i^{(k,l)} \middle| \Omega^{-1} H \Omega \middle| \Phi_j^{(k,l)} \right\rangle \tag{I.113}$$

$$or, H_{eff}^{(p,h)} = P^{(p,h)} \Omega^{-1} H \Omega P^{(p,h)} \tag{I.114}$$

Ω^{-1} in Equation (I.114), may not exists. Thus, to define effective Hamiltonian we have to adopt Bloch's equation approach (Equation (I.88). This approach eliminates Ω^{-1}.

In Bloch approach we solve following equation to obtain Ω and H_{eff} :

$$\begin{gathered} P^{(k,l)} \left[H\Omega - \Omega H_{eff}^{(k,l)} \right] P^{(k,l)} = 0 \\ Q^{(k,l)} \left[H\Omega - \Omega H_{eff}^{(k,l)} \right] p^{(k,l)} = 0 \\ \forall k = 0,1,....,p; \;\; l = 0,1,....,h \end{gathered} \tag{I.115}$$

Normalization condition is specified indirectly through parameterization of Ω. For CMS, intermediate normalization scheme is applied.

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

$$H_{eff}^{(p,h)} C^{(p,h)} = C^{(p,h)} E \tag{I.116}$$

$$\tilde{C}^{(p,h)} H_{eff}^{(p,h)} = E \tilde{C}^{(p,h)} \tag{I.117}$$

$$\tilde{C}^{(p,h)} C^{(p,h)} = C^{(p,h)} \tilde{C}^{(p,h)} = 1 \tag{I.118}$$

There is no contraction between different cluster amplitudes within the exponential, leading to partial hierarchical decoupling of cluster equations. This is known as sub-system embedding condition (SEC). Lower valence cluster equations are completely decoupled from the higher valence cluster equation, because of SEC. Thus to solve Bloch's equation for a particular sector, it is necessary to solve progressively from the lowest valence (0, 0) sector (*i.e.* SRCC sector) upwards up to (p, h) valence sector, and the lower valence sectors will appear as a constant in the higher valence sector.

I.9.D.iii. State-specific multi-reference coupled cluster theory (SSMRCC):

In state specific multi-reference coupled cluster (SSMRCC) [101-106] formalism, the wave operator is partitioned into two parts, *viz*, $e^{T^{(ext)}}$ and $e^{T^{(\mathrm{int})}}$. $e^{T^{(\mathrm{int})}}$ acts on a suitably chosen single-determinantal reference function ($|\Phi_0\rangle$) to generate the model space reference-function ($|\Phi^{\mathrm{int}}\rangle$) consists of model space determinants. $e^{T^{(ext)}}$ creates virtual space excitations from all model space determinants. The reference determinant $|\Phi_0\rangle$ can vary, depending upon various states. The exact function is generated as:

$$|\Psi\rangle = e^{T^{(ext)}}|\Phi^{\mathrm{int}}\rangle = e^{T^{(ext)}}e^{T^{(int)}}|\Phi_0\rangle \tag{I.119}$$

$e^{T^{(ext)}}$ and $e^{T^{(\mathrm{int})}}$ are mutually commutative, hence the SSMRCC theory can be considered as a direct generalization of the standard single reference CC theory. The correlation energy and T amplitudes in this method are as follows:

$$\langle\Phi_0|\left[H_N e^{T^{(ext)}}e^{T^{(int)}}\right]|\Phi_0\rangle = \varepsilon_{corr} \tag{I.120}$$

$$\langle\Phi^*|\left[H_N e^{T^{(ext)}}e^{T^{(int)}}\right]|\Phi_0\rangle = 0 \tag{I.121}$$

In deriving the above formulas, intermediate normalization $\left(\langle\Psi|\Phi_0\rangle = 1\right)$ is considered. Φ^* is any excited determinant. H_N is normal ordered Hamiltonian, *i.e.*, $H_N = H - \langle\Psi_0|H|\Psi_0\rangle$, consists of one $\left(F_N\right)$ and two body $\left(V_N\right)$ operators.

To tackle the quasi-degeneracy problem, linearized form for the $e^{T^{(\text{int})}}$ is used and the $e^{T^{(ext)}}$ is kept intact [249]. Resulting ansatz assumes the following form:

$$|\Psi\rangle = e^{T^{(ext)}}\left(1 + C^{(\text{int})}\right)|\Phi_0\rangle \tag{I.122}$$

The equations for the amplitudes are linear in terms of $C^{(\text{int})}$. If $e^{T^{(int)}}$ includes all possible excitations within the active orbital space, $e^{T^{(int)}}|\Phi_0\rangle$ and $\left(1 + C^{(\text{int})}\right)|\Phi_0\rangle$ wave functions are completely equivalent and only practical reasons may determine which approach will be more effective and convenient in a particular case.

I.9.D.IV. Multi-reference Brillouin-Weigner coupled cluster theory (MRBWCC):

As per our previous discussion we have seen that in the HSMRCC method, each reference determinant is related with distinct cluster operator [118]. In the SUMRCC approach, all the states are obtained simultaneously, but these methods suffer from the intruder state problem, resulting in serious convergence problem. FSMRCC methods [99, 109, 110, 120, 121] adopt the concept of common vacuum. In the SSMRCC [101-106] method, only one state is studied at a time, and the intruder state problem can be tackled very efficiently.

By denominator shifting the intruder state problem is handled by the multi-reference Brillouin Wigner coupled cluster [MRBWCC] theory [244, 245, 250-252]. The cluster equations are relatively simple and close resemblance to the SRCC problem, that's why converges smoothly. Major drawback of MRBWCC is that in the method suffers from size-extensivity problems. That's why for large systems posteriori corrections [252, 253] are necessary, but this method can be applied successfully to study diatomic to mid-sized molecules [254, 255].

In MRBWCC the model space spanned by M reference configuration Φ_μ. As a general function within the model space, reference state can be written as a linear combination of these configurations and can be expressed as:

$$\left|\Psi_\omega^P\right\rangle = \sum_{\mu=1}^{M} C_\mu^P \left|\Phi_\mu\right\rangle \tag{I.123}$$

ω is the chosen state, P is the projection operator. Exact wave function can be expressed in terms of the wave operator, Ω_ω as follows:

$$\left|\Psi_\omega\right\rangle = \Omega_\omega \left|\Psi_\omega^P\right\rangle \tag{I.124}$$

For the sake of simplicity ω is dropped from Ω_ω.

The wave operator is augmented with the Jeziorski and Monkhorst ansatz:

$$\Omega_\omega = \sum_{\mu=1}^{M} e^{S(\mu)} \left|\Phi_\mu\right\rangle \left\langle\Phi_\mu\right| \tag{I.125}$$

$S(\mu)$ is global excitation operator, defined with respect to the μ-th reference determinant. $S(\mu)$ consists of cluster operator $T(\mu)$ and the $F12$ part is $R(\mu)$ [256]. Thus $S(\mu)$ can be expressed as sum of $T(\mu)$ and $R(\mu)$:

$$S(\mu) = T(\mu) + R(\mu) \tag{I.126}$$

Expression for $R(\mu)$ is:

$$R(\mu) = R_1(\mu) + R_2(\mu) = C_k^i(\mu)\tilde{R}_i^k(\mu) + \frac{1}{4}C_{kl}^{jj}(\mu)\tilde{R}_{ij}^{kl}(\mu) \tag{I.127}$$

$$\tilde{R}_i^k(\mu) = \tilde{F}_{\alpha j}^{kj}(\mu)\tilde{a}_i^{\alpha}(\mu) \equiv F_{\alpha}^{k}(\mu)\tilde{a}_i^{\alpha}(\mu) \tag{I.128}$$

$$\tilde{R}_{ij}^{kl}(\mu) = \frac{1}{2}\tilde{F}_{\alpha\beta}^{kl}(\mu)\tilde{a}_{ij}^{\alpha\beta}(\mu) + F_{\alpha b}^{kl}(\mu)\tilde{a}_{ij}^{\alpha b}(\mu) \tag{I.129}$$

Here p, q, r indices corresponds to general spin orbitals, i, j, k are occupied spin-orbitals, a, b, c are for virtual counterpart. $C_{k....}^{i....}$ are parameters to be determined. $\tilde{a}$ are normal ordered replacement operators with respect to the pertinent references, and the matrix elements, $F_{kl}^{\alpha\beta}(\mu)$ corresponds to integrals over the correlation factor, $f_{12}(r_{12})$

$$F_{kl}^{\alpha\beta}(\mu) = \langle kl | f_{12}(r_{12}) | \alpha\beta \rangle \tag{I.130}$$

Exact energy can be obtained as an eigen value of the effective Hamiltonian. The eigen value equation can be written as:

$$\sum_{\nu} H_{\mu\nu}^{eff} C_{\nu}^{\omega} = E^{\omega} C_{\mu}^{\omega} \tag{I.131}$$

For CMS, cluster amplitudes corresponding to excitations within the model space are set to zero and assuming intermediate normalization, the remaining cluster amplitudes are obtained by solving cluster equations.

$$\begin{aligned}&\left(\varepsilon_{\omega}-H_{\mu\nu}^{eff}\right)\left\langle\Phi_{\nu}^{(\mu)}\middle|e^{S(\mu)}\middle|\Phi_{\mu}\right\rangle=\\&\left\langle\Phi_{\nu}^{(\mu)}\middle|\left[H_{N}\left(\mu\right)e^{S(\mu)}\right]_{connected}\middle|\Phi_{\mu}\right\rangle+\\&\left\langle\Phi_{\nu}^{(\mu)}\middle|\left[H_{N}\left(\mu\right)e^{S(\mu)}\right]_{Disconnected,Linked}\middle|\Phi_{\mu}\right\rangle\end{aligned} \tag{I.132}$$

I.10. Calculation of properties using derivative of energy:

Stationary state energies are important. However, in chemistry, quantities of interest are difference of energies, *i.e.*, binding energy, dissociation energy, ionization potential (IP), electron affinity (EA), etc. Most of spectroscopy involves change of energy in the presence of external field, like, electric or magnetic field. The change of energy due to external perturbation is also known as molecular properties.

Expectation value approach is useful only for first order peoperties. According to quantum mechanics, any first order property can be obtained using expectation value approach, *i.e.*,

$$D=\frac{\langle\Psi|\mu|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{I.133}$$

When an atom or a molecule is placed in an external field, if the field is small, then energy, wave function can be expressed as Taylor series expansion and each derivative of energy is associated with properties. For small perturbation, we can expand the change of energy and wave function with respect to the perturbatation field as a Taylor series expansion:

$$E(g) = E_0 + gE^{(1)} + g.g\frac{E^{(2)}}{2!} + ...$$

$$\Psi(g) = \Psi_0 + g\Psi^{(1)} + g.g\frac{\Psi^{(2)}}{2!} + ... \tag{I.134}$$

Where, $E^{(1)} = \left.\frac{\partial E}{\partial g}\right|_{g=0}$ and $E^{(2)} = \left.\frac{\partial^2 E}{\partial g^2}\right|_{g=0}$ are first and second derivative of energy with respect to the field (g). $\Psi^{(1)} = \left.\frac{\partial \Psi}{\partial g}\right|_{g=0}$, $\Psi^{(2)} = \left.\frac{\partial^2 \Psi}{\partial g^2}\right|_{g=0}$ are derivative of wave function with respect to field. These properties are referred as response properties [3, 155, 257]. Using Hellmann-Feynman theorem (HFT) [258-260] these properties can be defined [3]. The general expression for HFT can be written as:

$$\frac{\partial E(g)}{\partial g} = \frac{\left\langle \Psi_0 \right| \frac{\partial H(g)}{\partial g} \left| \Psi_0 \right\rangle}{\left\langle \Psi_0 \middle| \Psi_0 \right\rangle} \tag{I.135}$$

For response properties the expression of the perturbed Hamiltonian is:

$$H(g) = H - d \bullet g = H - \sum_{i=1}^{3} d_i g_i \tag{I.136}$$

g is field applied. This field should be weak, so that time-independent perturbation is applicable.

The derivatives of energy can be calculated using

A) Numerical or finite field approach.

B) Analytic approach.

In the next two subsections we shall discuss briefly about the two methods:

I.10.A. Finite field approach:

From computational point of view the simplest and the most straight forward way to calculate various energy derivatives is the finite field method. In this approach, any energy derivative is obtained by numerical difference of energies for different perturbation values. Using various methods finite field calculations were performed for the multipole moment [261-265], like, multipole polarizability [261-264, 266] and hyperpolarizability [267-269] etc. Accuracy of these calculations is dependent on the accuracy of energy. The method is convenient but the method suffers from accuracy problem to be precise, the method is unsatisfactory for higher order properties.

I.10.B. Analytic approach:

In analytical approach explicit expression of energy derivatives are solved. Analytic energy derivatives are desirable from the point of view of getting accurate higher order properties, and shows significant progress in last few decades. Analytic derivative packages with respect to nuclear parameters, as well as external fields have been developed at different levels of sophistications.

I.11. Calculation of linear response for molecules using coupled cluster theory:

Coupled cluster based linear response theories (CCLRT) were developed by various authors. A time dependent formalism was given by Monkhorst [90] and was later extended by Dalgaard and Monkhorst [257] and Koch *et al*. [127a, 148c] Mukherjee and Mukherjee [270] as well as Ghosh *et al,* [271] gave time independent version of the response approach. The original equations of Monkhorst incorporated only the change of the cluster amplitudes with respect to the external perturbation. Bartlett and co-workers [147] introduces orbital changes with respect to perturbation parameters. Thus, the method of Bartlett and co-workers [147] is suitable for gradients where orbital response is very important. First analytic linear response approach was developed by Monkhorst [90, 257] within coupled cluster framework. The perturbed Hamiltonian $H^{(1)}$ is written as:

$$H^{(1)} = gO \tag{I.137}$$

g, the perturbation strength, and O is the uniform external field operator. Total Hamiltonian can be written as:

$$H(g) = H_0 + gO \tag{I.138}$$

The expression for energy and cluster amplitude becomes:

$$H_N(g)e^{T(g)}\left|\Phi_0\right\rangle = \varepsilon_{corr}(g)e^{T(g)}\left|\Phi_0\right\rangle \tag{I.139}$$

$$\varepsilon_{corr}(g) = \left\langle\Phi_0\right|e^{-T(g)}H_N(g)e^{T(g)}\left|\Phi_0\right\rangle \tag{I.140}$$

$$\left\langle\Phi^*\right|e^{-T(g)}H_N(g)e^{T(g)}\left|\Phi_0\right\rangle = 0 \tag{I.141}$$

Expanding the energy and cluster amplitude by Taylor series expansion around zero perturbation strength and derivative of correlation energy and amplitude equations can be derived:

$$\varepsilon^{corr(1)} = \left\langle \Phi_0 \middle| e^{-T} \left\{ O + \left[H, T^{(1)} \right] \right\} e^{T} \middle| \Phi_0 \right\rangle \tag{I.142}$$

$$\left\langle \Phi^* \middle| e^{-T} \left\{ O + \left[H, T^{(1)} \right] \right\} e^{T} \middle| \Phi_0 \right\rangle = 0 \tag{I.143}$$

To solve Equation (I.142) we need derivative of the cluster amplitudes, which is obtained by solving Equation (I.143) and need to be solved for every mode of perturbation, which is computationally very tedious. Since SRCC is a non-variational theory, so it cannot take the advantages of the generalized HFT and (2n+1)-rule [148c, 272] for variation theory.

The problem can be overcome by the following two methods:

A) Z-vector method.

B) Constrained variational approach.

C) Stationary response approach.

We shall briefly discuss below the two methods.

I.11.A. Z-vector method:

This method was introduced first by Schaefer [273] for CI method, and Bartlett and co-workers [147] implemented for SRCCSD, which is based on interchange theorem of Dalgarno [274]. Rewriting Equations (I.142) and (I.143) in another form:

$$\varepsilon^{corr(1)} = Y^T T^{(1)} + Q(O) \tag{I.144}$$

$$0 = AT^{(1)} + B(O) \tag{I.145}$$

Where,

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

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

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

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

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

$$Z^T A = Y^T \tag{I.146}$$

Substituting Equation (I.141) in Equation (I.140) we get:

$$\varepsilon^{corr(1)} = Z^T B(O) + Q(O) \tag{I.147}$$

Equation (I.146) is a linear equation and contains no perturbation term and solution yields the Z-vector. This method is advantageous in the sense that, previously we have to solve Equation (I.145) for every mode of perturbation, but Equation (I.147) has to solve only once and store it. The term containing non-perturbative term is calculated for (3N-6) times. This procedure is conceptually simple, but a bit cumbersome for higher order properties.

I.11.B. Constrained variational approach:

Constrained variational approach (CVA) is based on the Lagrange's unknown multiplier method. This method is introduced to calculate derivative of energy with respect to perturbation in the SRCC framework by Jørgensen *et al,* [102a, 102c, 275].

This method involves construction of a functional with undetermined Lagrange multipliers λ_q. Corresponding SRCC equations can be written as:

$$\Im = \langle \Phi_0 | e^{-T} H e^{T} | \Phi_0 \rangle + \sum_{q \neq 0} \lambda_q \langle \Phi_q | e^{-T} H e^{T} | \Phi_0 \rangle \qquad \text{(I.148)}$$

If we vary $\Im$ with respect to all the parameters, *i.e.*, T and λ_q and setting them to zero, which is essential condition for variation, we have:

$$\frac{\partial \Im}{\partial T} = 0$$
$$\qquad \text{(I.149)}$$
$$\frac{\partial \Im}{\partial \lambda_q} = 0 \quad \forall \lambda_q$$

First we vary with respect to λ_q, we have:

$$\langle \Psi^* | e^{-T} H e^{T} | \Phi_0 \rangle = 0 \qquad \text{(I.150)}$$

This term does not contain any λ_q term.

Again, when we differentiate with respect to T, we will get λ_q term.

$$\frac{\partial \Im}{\partial T} = \langle \Phi^* | e^{-T}(-T) H e^{T} + e^{-T} H (-T) e^{T} | \Phi_0 \rangle +$$

$$\sum_q \lambda_q \langle \Phi_q | e^{-T}(-T) H e^{T} + e^{-T} H (-T) e^{T} | \Phi_0 \rangle \qquad \text{(I.151)}$$

$$\frac{\partial \Im}{\partial T} = \langle \Phi^* | e^{-T} [H, T] | \Phi_0 \rangle + \sum_q \lambda_q \langle \Phi_q | e^{-T} [H, T] e^{T} | \Phi_0 \rangle$$

One thing to mention here is that, in variational case we normally do expectation value, but such attempts in CC would lead to an infinite terminating series. But if we solve in this manner, we shall get variational expression.

Derivative with respect to λ_q, gives solution for T, and λ_q can be calculated for derivative with respect to T

$$\frac{\partial \Im}{\partial \lambda_q} = \left\langle \Phi_q^* \middle| e^{-T}\left[H,T\right] \middle| \Phi_0 \right\rangle + \sum_q \lambda_q \left\langle \Phi_q \middle| e^{-T}\left[H,T\right] e^{T} \middle| \Phi_0 \right\rangle \qquad \text{(I.152)}$$

If we compare with the Z-vector method, we will see that the terms on the RHS are same as CVA methods.

In this formulation obtaining derivative for expressions for higher order derivative is quite simpler. The cluster amplitude derivatives obey the (2n+1) rule, but the derivatives of Lagrange multipliers obey (2n+2)-rule [148c, 272].

I.11.C. Stationary response approach:

In stationary response approach Hellmann-Feynman theorem is satisfied. Thus, stationary approach is naturally suitable for the calculation of properties. In this approach the energy functional is defined and is made stationary with respect to the ground state cluster amplitudes. It was shown by Pal and coworkers [276, 277] that if cluster amplitudes and their derivatives are truncated to uniform degree, then the stationarity condition

$$\frac{\partial E^{(i)}}{\partial t^{(j)}} = 0 \qquad \text{(I.153)}$$

leads to identical set of equations for a fixed value of $i-j$. The derivative cluster amplitudes are obtained by making the derivative energy functional stationary with respect to unperturbed or ground state cluster amplitudes. The stationary approach leads to (2n+1)-rule with the help of first derivative of cluster amplitudes we can calculate the third order properties. XCC, UCC and

ECC are the popular energy functionals used. However, the problem of the stationary response approach is that the functional is non terminating and needs to be truncated for practical application. Except ECC functional XCC and UCC also gives disconnected diagrams leading to loss of size extensivity. ECC being double linked functional this problem is eliminated naturally.

I.12. MRCC response approach

MRCC methods are well established for the calculation of energies of quasi degenerate systems. Depending on the way the non dynamic correlation is introduced the methods are divided into various sub classes. Though response approach for closed shell systems existed for quite some time, similar development with multi-reference based methods is very recent. Formulation of energy derivatives using multiroot coupled cluster methods is a challenging task. Monkhorst's [90, 257] linear response approach was extended for the multi root problem by Pal and co-workers [49, 50, 145]. This approach was implemented for first derivatives when perturbation is electric field [49, 50, 145]. However, this approach is not suitable as it requires first derivative of the cluster amplitudes for first derivative of energy. Lagrange based linear response approach for the specific root of the effective Hamiltonian, was developed by Pal and co-workers [51, 150] within the MRCC framework. This approach was formulated for the Hilbert space [51a] as well as Fock-space [51b] methods. The formulation is very general and can be implemented for any method. Szalay [67] independently formulated similar approach for a complete model space using Lagrange multipliers for the FSMRCC method. Theory of analytic gradients within EOMCC framework was developed by Stanton [68] using energy derivatives and implemented by stanton and gauss [69]. Nooijen and co-workers [143] implemented analytic gradients within STEOMCC using Lagrange based approach. Recently, Krylov and co-workers [71] developed and implemented the Lagrange based response approach within Lagrange framework for the spin flip EOMCC. Analytic gradients for SAC-CI [58], CI [57, 61, 69], MRCI [63], propagators [64] and RI-CC2 [62] are available in the literature.

I.12.A. Z-vector method for FSMRCC response:

Within FSMRCC frame work the Z-vector method was implemented by Ajitha *et al*. [145, 49, 50]. Here we discuss briefly about the method.

The formalism of Z-vector technique is same as used in SRCC method. In this method effective Hamiltonian H_{eff} is introduced instead of normal Hamiltonian. The H_{eff} is defined within model space. In presence of field eigen value equation for H_{eff} becomes:

$$\sum_i \left[H_{eff}(g)\right]_{ji} C_{i\mu}(g) = E_\mu(g) C_{j\mu}(g) \qquad \text{(I.154)}$$

Where, $C_{j\mu}(g)$ and $E_\mu(g)$ are the field-dependent model space coefficients and energies of the states of the interest.

For deriving the response equations, the relevant field-dependent quantities are expanded as a Taylor series expansion in g:

$$\begin{aligned}
\Omega(g) &= \Omega^{(0)} + \Omega^{(1)} g + \frac{1}{2!}\Omega^{(2)} g^2 + \ldots. \\
H_{eff}(g) &= H_{eff}^{(0)} + H_{eff}^{(1)} g + \frac{1}{2!} H_{eff}^{(2)} g^2 + \ldots. \\
E_{\mu}(g) &= E_{\mu}^{(0)} + E_{\mu}^{(1)} g + \frac{1}{2!} E_{\mu}^{(2)} g^2 + \ldots. \\
C_{j\mu}(g) &= C_{j\mu}^{(0)} + C_{j\mu}^{(1)} g + \frac{1}{2!} C_{j\mu}^{(2)} g^2 + \ldots.
\end{aligned} \tag{I.155}$$

$\Omega^{(0)}$, $H_{eff}^{(0)}$, $E_{\mu}^{(0)}$, $C_{j\mu}^{(0)}$ are wave-operator, effective Hamiltonian, exact energies and the model space coefficients of the field free situation.

The Bloch equation (Equation (I.88)) in the absence of any external perturbation is given by:

$$P\left[H\Omega^{(0)} - \Omega^{(0)} H_{eff}^{(0)}\right]P = 0 \tag{I.156}$$

$$Q\left[H\Omega^{(0)} - \Omega^{(0)} H_{eff}^{(0)}\right]P = 0 \tag{I.157}$$

Analytic response of the Bloch equation at each order in g can be obtained from the derivatives of the Bloch equation evaluated at zero field.

$$\frac{\partial}{\partial g} P\left[H(g)\Omega(g) - \Omega(g) H_{eff}^{(0)}(g)\right]_{g=0} P = 0 \tag{I.158}$$

$$\frac{\partial}{\partial g} Q\left[H(g)\Omega(g) - \Omega(g) H_{eff}(g)\right]_{g=0} P = 0 \tag{I.159}$$

These equations describe the analytic response of the wave operator and the effective Hamiltonian to the weak external field. Similarly closed algebraic equations may thus be derived for response at each order in g. While solving Equation (I.158) and Equation (I.159), we hold the unperturbed quantities, *i.e*, H_{eff}, Ω obtained from Equation (I.156) and Equation (I.157) constant. We obtain the first derivative of the effective Hamiltonian from the solution of Equation (I.158).

Equation (I.158) and Equation (I.159) for one valance can be written as:

$$\begin{aligned}&P^{(0,1)}\left(\bar{H}^{(1)}+\left[\bar{H}^{(1)},T^{(0,1)}\right]+\left[\bar{H},T^{(0,1)(1)}\right]\right)P^{(0,1)}\\&=P^{(0,1)}H_{eff}^{(1)(0,1)}P^{(0,1)}\end{aligned} \tag{I.160}$$

$$\begin{aligned}&Q^{(0,1)}\left(\bar{H}^{(1)}+\left[\bar{H}^{(1)},T^{(0,1)}\right]+\left[\bar{H},T^{(0,1)(1)}\right]-\right.\\&\left.\left[T^{(0,1)},H_{eff}^{(0,1)(1)}\right]-\left[T^{(0,1)(1)},H_{eff}^{(0,1)(1)}\right]\right)P^{(0,1)}=0\end{aligned} \tag{I.161}$$

It can be seen that derivative cluster amplitudes are required to get derivative effective Hamiltonian. Following SRCC Z-vector approach the final expression for the $H_{eff}^{(1)}$ is:

$$\begin{aligned}&P^{(0,1)}H_{eff}^{(0,1)(1)}P^{(0,1)}=\\&P^{(0,1)}\left(\bar{H}^{(1)}+\bar{H}^{(1)}T^{(0,1)}\right)P^{(0,1)}+\\&Q^{(0,1)}\xi^{(0,1)}Q^{(0,1)}Q^{(0,1)}\bar{H}^{(1)}P^{(0,1)}\end{aligned} \tag{I.162}$$

Equation (I.161) is a result of interchange theorem. Thus, the derivative effective Hamiltonian is written in terms of ξ-amplitudes and is independent of derivative $T^{(0,1)}$ amplitudes. The equation for $\xi^{(0,1)}$ is perturbation independent and hence needs to be solved only once. However, derivative of $T^{(0,0)}$ amplitudes do appear explicitly.

I.12.B. Constrained variational approach within FSMRCC one valance problem:

The constrained variational approach (CVA) for Hilbert space [51a] and Fock space [51b] was developed by Shamsunadar *et al*. [51]. Here we shall discuss only the CVA approach within FSMRCC framework for ionized states, *i.e.*, (0,1) sector. The formalism for electron attached state is same, but the electron attached state is obtained by reverting hole-particle indices.

The valence universal wave operator, Ω is defined as:

$$\Omega = \left\{ e^{T^{(0,0)}} e^{T^{(0,1)}} \right\}$$

The equation for cluster amplitude and effective Hamiltonian are obtained by solving Equation (I.156) and Equation (I.157)

The H_{eff} and Ω are obtained by solving the equations. The diagonalization of the effective Hamiltonian yields the roots, which are the energies of the corresponding exact states. As a result of normal ordering, subsystem embedding condition (SEC) [99] holds due to which, one can systematically solve for the cluster amplitudes starting from the zero valence (0,0) sector of FS upwards upto the desired valence sector.

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

$$E_{\mu} = \sum_{ij} \tilde{C}^{(0,1)}_{\mu i} \left(H_{eff} \right)^{(0,1)}_{ij} C^{(0,1)}_{j\mu} \tag{I.163}$$

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

$$\Im = \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} \left(H_{eff}\right)_{ij}^{(0,1)} C_{j\mu}^{(0,1)} +$$

$$P^{(0,1)}\Lambda^{(0,1)}Q^{(0,1)}Q^{(0,1)}\left[H\Omega - \Omega H_{eff}^{(0,1)}\right]P^{(0,1)} + \tag{I.164}$$

$$P^{(0,0)}\Lambda^{(0,0)}Q^{(0,0)}Q^{(0,0)}H\Omega P^{(0,0)} +$$

$$E_{\mu}\left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)} C_{j\mu}^{(0,1)} - 1\right)$$

For singles double approximations $\Lambda^{(0,1)} = \Lambda_1^{(0,1)} + \Lambda_2^{(0,1)}$ and $\Lambda^{(0,0)} = \Lambda_1^{(0,0)} + \Lambda_2^{(0,0)}$

In Equation (I.164) $\Lambda's$ are Lagrange multipliers. For complete model space (CMS), H_{eff} has an explicit expression in terms of cluster operators, resulting the fact that the closed part of the Lagrange multiplier vanishes. Thus, the above Equation reduced to:

$$\Im_{opt}^{(0)} = \left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(0)} C^{(0,1)(0)}\right)_{\mu\mu} \tag{I.165}$$

Differentiating Equation (I.164) with respect to Λ gives the cluster amplitudes. The equations for Ω-amplitudes are decoupled from the Λ amplitudes. On the other hand to evaluate Λ amplitude Ω amplitudes are required. The Lagrangian is defined in Equation (I.164) can be differentiated with respect to the field g, to obtain the derivative Lagrangians at every order. The zeroth order and the first order Lagrangian can therefore be written as:

$$
\begin{aligned}
&\Im^{(1)} = \left(\tilde{C}^{(0,1)(1)} H_{eff}^{(0,1)(0)} C^{(0,1)(0)}\right)_{\mu\mu} + \left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(1)} C^{(0,1)(0)}\right)_{\mu\mu} + \\
&\left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(0)} C^{(0,1)(1)}\right)_{\mu\mu} + \\
&P^{(0,1)} \Lambda^{(0,1)(1)} \left[H^{(0)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{(0,1)(0)} \right] P^{(0,1)} + \\
&P^{(0,1)} \Lambda^{(0,1)(0)} \left[H^{(1)} \Omega^{(0)} + H^{(0)} \Omega^{(1)} - \Omega^{(1)} H_{eff}^{(0,1)(0)} - \Omega^{(0)} H_{eff}^{(0,1)(0)} \right] P^{(0,1)} + \\
&P^{(0,1)} \Lambda^{(0,1)(1)} H^{(0)} \Omega^{(0)} P^{(0,1)} + P^{(0,0)} \Lambda^{(0,0)(0)} H^{(1)} \Omega^{(0)} + H^{(0)} \Omega^{(1)} P^{(0,1)} \\
&E_{\mu}^{(0)} \sum_{ij} \left(\tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(1)} + \tilde{C}_{\mu i}^{(0,1)(1)} C_{j\mu}^{(0,1)(0)} \right) - E_{\mu}^{(1)} \left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)(0)} C_{j\mu}^{(0,1)(0)} - 1 \right)
\end{aligned}
\tag{I.166}
$$

Equation (I.164) and Equation (I.166) gives the energy and the first order energy derivative for the μ-th state. Because of stationarity of Lagrangian with respect to Λ and Ω, the above expressions are further simplified. The energy derivatives follow (2n+1) rule with respect to the Λ-amplitudes and (2n+2)-rule with respect to the Ω-amplitude. The (2n+1) rule for the eigen vectors $\tilde{C}^{(0,1)}$ and $C^{(0,1)}$ for evaluation of energy derivatives. With this the expression for derivative Lagrangian simplifies to:

$$
\begin{aligned}
&\Im_{opt}^{(1)} = \left[\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(1)} C^{(0,1)(0)} \right]_{\mu\mu} + \\
&P^{(0,1)} \Lambda^{(0,1)(0)} \left[H^{(1)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{(0,1)(1)} \right] P^{(0,1)} + \\
&P^{(0,0)} \Lambda^{(0,0)} H^{(0)} \Omega^{(0)} P^{(0,0)}
\end{aligned}
\tag{I.167}
$$

The CVA method is a single-root method. The Λ amplitudes depend on the desired state of the molecule. Therefore, for every state one has to calculate the Λ amplitudes separately. In contrast, the non-variational response of

FSMRCC [144] has a multiple-root structure. However, the expensive evaluation of wave-function derivatives for each mode of perturbation is avoided in CVA-FSMRCC. Also, the single-root feature makes CVA more attractive for the cases like curve-crossing studies of excited states, etc. than the non-variational response method. It can be seen that the Λ-equations for one-valence problem are same as the zeta equations. in the EOMCC method [126, 141].

I.13. Electronic resonance:

When an electron collides with a molecule various possibilities occur during their collision process. This includes elastic or inelastic scattering, excitation of electronic and/or nuclear states of the molecule, dissociative attachment, ionization. However, at low energy range below 10 eV scattering is possibile. In an elastic scattering energy of the particle is conserved. In a non-elastic scattering exchange of energy between the electron and target molecule happens and the energy of the outgoing electron is either less or more than the incident electron. During electron molecule scattering the electron can get trapped in the attractive potential of the target molecule and never come out of the attractive potential well. To avoid this possibility the potential at the origin should be less attractive than $V(r) = -r^{-2}$. In another possibility, due to multiple scattering, electron is temporarily trapped by the target and eventually comes out. In order to have free particle in and out at the infinity the interaction potential of the target molecule should fall off quicker than r^{-3} at infinity. This is called as the direct scattering. During the direct scattering process when the life time of the compound system is larger then the collision time the phenomenon is called as a resonance. Resonance scattering involves formation of a metastable or a quasi bound state with sufficiently long life which eventually decays into open channels. Resonance phenomena constitutes some of the most interesting features of scattering experiments. In this thesis we have considered the shape resonance phenomena associated with the elastic scattering (where the kinetic energy is conserved before and after collision).

The electronic wave function of the resonant state has large amplitude within the target molecule at some incident energies. This is possible when the incident energy falls in one of the discrete bands, where the incident electron finds a comfortable quasi stationary orbit in the field of target molecule. The effective potential in the target molecule is made up of attractive potential (at small distances) combined with a repulsive potential (at long distances) which produces a barrier in the potential. For energies below the maximum in the barrier, there would be bound states inside the attractive part of the potential if tunneling can be ignored. However, quantum mechanical tunneling permits particle to be ‘trapped’ inside the attractive part of the potential to escape to infinity, and the tunneling rate depends on the height and thickness of the barrier. Larger *l* values causes bigger centrifugal barriers, making resonance narrower and thus suppressing tunneling. Once the electron has entered the region inside the barrier, it will take some time before the electron can come out by tunneling effect. This type of resonance is called shape resonance or potential resonance. Since the resonance state is produced by an appropriate shape of the effective interaction potential between the electron and the molecule.

In the presence of the inelastic channels, electron transfers part of the energy in exciting the target molecule. If the energy of the incident electron is large enough, then after the excitation its energy becomes negative and it coincides with one of the bound state energies of the excited target molecule. It can escape only after it gains sufficient energy and this takes some time before it could come out. This type of resonance is called as core-excited type I resonance or the Feshbach resonance [278].

Shape resonance associated with the effective potentials in the inelastic channel are called as core-excited type II resonance or core excited shape resonances.

Resonance states can be correctly described as states embedded in and interacting with the continuum. The resonance energy is complex and is given by:

$$E_{res} = E_R - i\frac{\Gamma}{2} \tag{I.168}$$

E_{res} is known as Siegert energy. Where, E_R is position of the resonance and Γ gives half width of the resonance. In resonance, the wave function of the outgoing electron is not square integrable. This makes the computation of the resonance wave function difficult. Thus, the bound state methods cannot be used to solve the resonance problem.

We are interested in the solution of the combined system *i.e,* an electron and a target molecules, which can be described by the Hamiltonian. By solving the time independent Schrodinger equation the energy of the system and wave function can be obtained. However, it is a many body problem and dynamic interaction of the electron with the target molecule does not allow us separation of variables. Thus we need to use some approximations to solve the problem. The final wave function has to be anti symmetric with respect to the exchange of the projectile electron and target electrons. Among various methods, we will discuss few of the approaches. There are various approaches for the calculation of resonance parameters they can be broadly divided into direct and indirect approaches. Siegert method [279], complex scaling [13-16], complex absorption potential [17, 18] optical potential method [280] are the direct methods. Whereas, stabilization method [19-21], time delay maximum analysis [281], S matrix parametrization [282] are indirect methods. The direct methods are more convenient to apply. The Siegert method [279] obtains resonance parameters as poles of the S matrix. In this approach any iterative diagonalization of the full matrix is avoided. However, the broad resonances may get hidden or masked by scattering poles regardless of the range of finite basis set used. In the close-coupling [283] approximation the scattering wave function is expanded as a truncated product function consisting of target and scattered electron function. The scattered electron function is a continuum function satisfying the appropriate boundary conditions in the asymptotic region. The phase shifts, as a function of energy, are obtained and are fitted to the Breit-Wigner formula [284-286] to get the energy and the width of the resonance.

The methods which treat resonance as a quasi bound state in the scattering continuum have their origin in the scattering theory. The potentials used initially were static potentials without any exchange or polarization. Later on they were included parametrically or by scaling the results to fit the experimental values. Apart from the standard scattering theory purely L^2 methods have been explored for the study of resonance problem. The Kohn and Schwinger variational approach is the earliest approach [287]. In the L^2 approach resonance state is obtained by diagonalization of the Hamiltonian once it is projected onto an L^2 basis set. In these methods asymptotic wave functions are not included. Apart from these methods, hybrid methods which use sacttering calculations as well as L^2 methods were used for the study of resonance. In these methods polarization of the target due to incoming electron, many body effects and non-adiabatic effects were successfully implemented. The T-matrix [288] and R-matrix [289] methods are very successful. The boomerang model [290, 291] derived resonance parameters using *ab initio* method.

In the direct scattering approach resonance is associated with the complex eigen value of the Hamiltonian. The Gamow-Siegert wave function is a solution of the Schrödinger equation with purely outgoing boundary condition. These boundary condition ensures that the eigen values are complex. These states are divergent and does not belong to the hermitian domain of the

Hamiltonian. In the inner region they resemble with a bound state and outside they represent decaying states. Thus, study of resonance using quantum methods requires simultaneous treatment of electron correlation and continuum effects. By changing the boundary conditions, the complex Hamiltonian of the (N+1) particle turns into a non-Hermitian Hamiltonian with eigen values of the Hamiltonian are real. However, Hamiltonian can be modified in such a way that the eigen values represent the Siegert energies. This modification of the Hamiltonian is obtained through analytic continuation method.

I.13.A. Complex scaling:

Balslev and Combes [13, 14] developed the complex scaling method, which simplified the theory of atomic and molecular resonance.

Complex scaling method involves similarity transformation. By applying unbounded similarity transformation to the original Hamiltonian (H) the resonance state becomes square integrable functions associated with the eigen function of a transformed Hamiltonian, UHU^{-1} [292].

$$\left(UHU^{-1}\right)\left(U\Psi_R\right)=\left(E_{res}-i\frac{\Gamma}{2}\right)\left(U\Psi_R\right) \qquad \text{(I.169)}$$

Such that:

$$U\Psi_R \to 0 \text{ as } r \to \infty$$

$U\Psi_R$ belongs to Hilbert space, but not Ψ_R. The unbounded similarity transformation is provided by complex scaling method. The original eigen spectrum is changed (some energy eigen spectrum may exist) and the complex scaled Hamiltonian losses its self-adjoint nature. The new set of eigen values may occur in the complex plane. The complex operator is expressed as:

$$U = e^{i\theta r\frac{\partial}{\partial r}} \tag{I.170}$$

For any analytic function, $f(r)$, we can operate U as:

$$Uf(r) = f\left(re^{i\theta}\right) \tag{I.171}$$

Complex scaling method compresses the information about the evolution of a resonance state at infinity into a small well defined part of the space. Resonance state involves single square integrable function and not collection of continuum eigen state of the unscaled Hermitian Hamiltonian. Using complex scaling the resonance wave function becomes square integrable.

Boundary condition distinguishes if a particular function is a bound state [L^2-function] or unbound/scattering state [non-L^2-function]. In complex scaling, for a particular value of $|\theta| \geq \Pi / 2$, the boundary condition of square integrability is conserved. On the other hand any other set of eigen functions of real eigen value would not appear as $r \to re^{i\theta}$. This implies that H and $H(\theta)$ have same real eigen values. If long range potential is used, then scattering wave functions (continuum solutions of H) are conserved, otherwise not. The radial scattering solution can be represented as linear combinations of $e^{(\pm ikr)/r}$, as $r \to \infty$. To maintain bound state, we have to take both $r \to e^{i\theta}$ and $k \to ke^{-i\theta}$, otherwise either of r or k will shoot up exponentially to ∞. If $k \to ke^{-i\theta}$, the corresponding energy eigen spectrum (E) for the allowed scattering energies become: $E = k^2 / 2 \to e^{-i2\theta}k^2 / 2$. This implies that the continuum is rotated into the lower half complex energy plane. In fact the continuous spectrum of $H(\theta)$ is different from H. From the above discussion we can write the following conclusions:

1) Bound state eigen values of $H(\theta)$ are independent of θ. If $|\theta| \leq \Pi / 2$, then $H(\theta)$ and H are identical.

2) Scattering threshold corresponds to the possibility of fragmentation of different system of different states of excitations, and independent of θ, $|\theta| \leq \Pi / 2$.

3) The continuous spectra of the original Hamiltonian (H) are rotated around their respective starting points by an angle of 2θ into the lower half plane. During this process, certain new discrete complex eigen values may come up in the lower half complex energy plane in the sector $0 > \arg\left(z - E_0^{thres}\right) \geq -2\theta$, z is complex energy and E_0^{thres} is the threshold scattering energy.

Although the complex scaling theory is valid for full molecular problem, but the method is valid for the centre of mass Hamiltonian of a system of particles interacting through the dilation analytic potentials. The complex scaling method is consistent with the Born-Oppenheimer approximation, which is very first approximation to study resonance. On the other hand, if we apply directly the Balslev and Combes theorem [13-15] for resonance study, then it will be very much impractical to use. Because in that case, the wave function will depend on nuclear and electronic coordinate.

Applying complex scaling method to molecular potential may lead to determining the electronic spectra for unphysical internuclear separations [293, 294]. In addition to that, handling complex nuclear distance is very difficult. Thus, it is better to fix the nuclei on the real axis and scale the electronic coordinate. This approximation reduces the mathematical effort and made easy for computational implementation. This approximation is known as complex coordinate real axis clamped nuclei approximation (CCRACNA). The difficulty arises to imply CCRACNA, when the nuclear coordinates are fixed in real axis and the electronic coordinate r_i is scaled as: $r_i \rightarrow r_i e^{i\theta}$, then the nuclear interaction will become: $\sum_{\alpha} \left| r_i e^{i\theta} - R_\alpha \right|^{-1}$. The nuclear interaction become non-analytic [295] because the argument of the absolute value can vanish for a continuous range of value, such that, $\left| r_i e^{i\theta} \right| = \left| R_\alpha \right|$ and dot products of the two radius vector will become: $r_i \cdot R_\alpha = \cos\theta$ and gives a continuous range line of square branch points, making the Hamiltonian non-analytic. This makes the Balslev-Combes theorem [13-15] inapplicable to BO Hamiltonian. To solve the problem, two different groups [296, 297] independently developed methods to implement CCRACNA in a practical manner. McCurdy and Rescigno [296] applied Gaussian basis functions, where only the exponents are scaled by a complex factor. These can also be back rotated by $e^{-i\theta}$. McCurdy and Rescigno [296] diagonalized the real Hamiltonian. The back rotated wave functions and a real Hamiltonian is equivalent to using real wave functions and a complex Hamiltonian. On the other hand Moiseyev and Corcoran [297] applied BO approximation. When the method of coordinate rotation is applied to such Hamiltonian, they kept the nuclear coordinate fixed and rotated only the electronic coordinate. Scaling only the electronic coordinate is advantageous for practical purpose. They have applied this method to study autoionizing states of H_2 and H_2^-. For this study they scaled only the electronic coordinates of BO Hamiltonian [297]. Simon [298] introduced smooth exterior scaling (SES), such that any interior non analyticities can be avoided, but the coordinates be on the real axis for long enough. In this case the exterior complex scaling operator can be written as:

$$\begin{aligned} U &= 1 && if \quad r < r_0 \\ &= e^{i\theta(r-r_0)\frac{\partial}{\partial r}} && if \quad r \geq r_0 \end{aligned} \tag{I.172}$$

Expression for Hamiltonian is:

$$\begin{aligned} H(\theta) &= H(r) && if \quad r < r_0 \\ &= H\left((r-r_0)e^{i\theta}\right) && if \quad r \geq r_0 \end{aligned} \tag{I.173}$$

Lipkin and co-workers [299] implemented the Simon's [298] method for model system using finite-basis set approximation. In this method, the basis is scaled. Thus for exterior scaling the orthonormal basis functions are given as:

$$\begin{aligned} \tilde{\Phi}_i &= \Phi_i(r) && if \quad r < r_0 \\ &= e^{-i\frac{\theta}{2}}\Phi_i\left((r-r_0)e^{-i\theta}+r_0\right) && if \quad r \geq r_0 \end{aligned} \tag{I.174}$$

Rom *et al*. [300] proposed another smooth exterior scaling (SES) which avoids the need of carrying out the analytical continuation of the potential term in the Hamiltonian into the complex coordinate plane. SES can be expressed as:

$$f(r) = \frac{\partial F(r)}{\partial r} = 1 + \left(e^{i\theta} - 1\right) g(r) \tag{I.175}$$

The path in the complex coordinate plane, $F(r)$ is defined as: $F(r) \rightarrow re^{i\theta}$ as $r \rightarrow \infty$ and $g(r)$ is a fraction. If $V(r \geq r_0)$, then the unscaled potential $V(r)$ can be used.

Moiseyev [301] derived SES Hamiltonian of having expression:

$$H = -\frac{\nabla^2}{2} + V(F(r)) + V_{CAP} \tag{I.176}$$

V_{CAP} is universal energy independent complex absorbing potential (CAP). If SES is applied, then the CAP has non-zero values in the region where interaction potential vanishes. Complex SES Hamiltonian is obtained by adding to the unscaled Hamiltonian matrix, which represents universal CAP.

For complex scaling, if a truncated basis $\phi = \{\phi_\mu\}$ of order M is used, then the following relation can be obtained:

$$\bar{H} = \bar{T} + \bar{V} \tag{I.177}$$

Here '-' denotes scaling. $\bar{H}$ contains large number of complex eigen values. The most impotant task is to find out which complex eigen value corresponds to resonance states. If we use complete basis set, and during the process, if we increase rotation angle θ, when resonance eigen value (E_{res}) is revealed, it will become independent of complex scale factor, $\eta = e^{i\theta}$. Such that:

$$\frac{\partial E_{res}}{\partial \eta} = \frac{\partial^2 E_{res}}{\partial \eta^2} = ... = 0 \qquad \text{(I.178)}$$

In practice we have to use a finite basis set of order M. Thus, E_{res} should be fairly necessary. To find E_{res} we have to adopt graphical method. Using various types of stabilization graph [302-304] finding E_{res} is possible.

If scaling operator satisfies $\left(U^{\dagger}\right)^{-1} = U^{*}$, then the transformed Hamiltonian becomes complex symmetric. This equality makes the resonance computationally feasible.

Complex scaling has been successfully applied to SCF method [305-307]. There are two different ways of approaches of applying in the SCF field:

1) McCurdy *et al*, [305, 306] adopted real Hamiltonian in augmentation with complex wave functions. In this method resonant eigen values were obtained by SCF method. This method is comparable to bound state SCF method.

2) Another approach used complex Hamiltonian with real basis functions. This method was proposed by Mishra *et al.* [307] Here the resonance eigen value can be calculated by a little bit modification of exsisting code. This method has also been applied to calculate resonance and width by using highly correlated method like FSMRCC [308].

Other than complex scaling method, finite box method have also drawn extra attention for studying resonance, in such cases the compound system becomes quasi-bound. The molecular Hamiltonian is perturbed by an appropriate complex potential, which enforces an absorbing boundary condition. This artificial potential absorbs the emitted particle and simultaneously transforms the former continuum wave function into a square integrable wave function. Jolicard and Austin [17, 309-311] applied CAP method for this purpose. The stability of resonance eigen value can also be achieved by varying the strength or the location of the absorbing potential [18, 312-314], whose job would be to absorb the perfectly outgoing Siegert state without creating any reflection [310]. Difficulty of using the are the conditions and approximations at which the spectrum of CAP augmented Hamiltonian resembles with the spectrum of complex scaled Hamiltonian.

I.13.B. Complex absorption potential (CAP):

Analytic continuation of the Hamiltonian can also be achieved using complex absorbing potential. CAP can easily be implemented with any quantum chemistry method. First application of CAP for resonance problem was by Jolicard and Austin [17] using Hazi-Taylor [19] potential model. In CAP method absorbing boundary conditions are introduced in region exterior to the target molecule. The CAP absorbes the outgoing electron and the wave function is made square integrable. Electron absorption is achieved by introducing or adding one particle potential to the Hamiltonian:

$$H(\eta) = H - i\eta W \tag{I.179}$$

η is real positive number, known as CAP strength and W is potential. Riss and Meyer [18] proved that when $\eta \frac{dE}{d\eta}$ is minimal the energy $E(\eta)$ is a Siegert energy.

$$E_{res} = E_R - i\frac{\Gamma}{2} \tag{I.168}$$

The eigen spectrum of a perturbed Hamiltonian:

$$H(\eta) = H - i\eta W(r) \tag{I.180}$$

The η independent Hamiltonian can be expressed as:

$$H = -\frac{1}{2}\frac{d^2}{dr^2} + V(r),\ \ \eta > 0 \tag{I.181}$$

$W(r)$ is continuous Coulomb potential. $\eta \to 0$, the eigen value of $H(\eta)$ converges towards the poles of the Green's function on its physical sheet, subject to the condtion that $\pi \geq 0 \geq \arg(E) \geq 0$. CAP becomes equivalent to complex scaling in the limit of $\eta \to 0^+$, which is impoosible for practical purpose. Because This limit can only be achieved only when complete basis set is used, but complete basis set is computationally expensive. The large value of η creates artificial reflections. Various correction scheme exsists in the literature to remove the artificial reflections [280, 309]. Assuming $W_0(r)$, which is twice differentiable and satisfies the following relations:

$$\begin{aligned} W_0(r) &= 0 \quad for \quad r \leq r_c \\ &> 0 \quad for \quad r > r_c \end{aligned} \tag{I.182}$$

$W_0^{'}(r) \geq 0$ and $W_0(r) \to \infty$ for $r \to \infty$, r_c is cut off parameter. For reflection-free CAP, the regular solution is identical to the exact Siegert resonance wave function upto r_c and E_0 is the exact Siegert resonance energy. This perturbation is not desired on the target and CAP is set to zero in the vicinity of the target. Riss and Meyer [312, 313] developed transformative CAP (TCAP). In exchange part it implies a modified kinetic energy instead of adding local complex potential. For cut-off potential TCAP and SES are identical. CAP methods are best for treating molecular electronic resonance [17, 315].

CAP method in augmentation with CI [316], electron propagator theories [317-319], MRCI [320-322], has been applied to study the resonance states in metastable ions. To calculate resonance energy and width, these methods involve difference of energy between ground state total energy of the [N±1] and neutral target. Resonance energy and width for the electron detachment (Auger resonance)/electron attachment shape resonance can be obtained simultaneously from the ionization potential/electron affinity studies. Taking the same idea we can apply CAP method to calculate resonance energy and width of meta-stable states within FSMRCC frame work. Sajeev *et al,* [31] developed correlated independent particle FSMRCC in augmentation with CAP (CAP-CIP-FSMRCC) method to calculate resonance energy and width of metastable state in an efficient manner. The method is briefly discussed below. Details will be described in chapter II.

To start with CAP-CIP-FSMRCC method, let us start with CAP-FSMRCC method. Then the advantage of CAP-CIP-FSMRCC method over CAP-FSMRCC will be clear.

In the CAP-FSMRCC approach for the resonance problem, electron absorption is achieved by adding the absorption potential to the Hamiltonian:

$$H(\eta) = H - i\eta W \tag{I.179}$$

The strength of the potential is defined as, η, W is local, non-negative, semi definite one particle potential. At $\lim_{\eta\to 0}$, $H(\eta)$ describes the analytic continuation of the Hamiltonian H. As discussed earlier in Section I.9.D.ii, that in FSMRCC method, the wave operator and the effective Hamiltonian are solved by using Bloch equation [234] (Equation I.88). For electron attached state Equation (I.88) can be written as:

$$P^{(1,0)}\left[H\Omega - \Omega H_{eff}^{(1,0)}\right]P^{(1,0)} = 0$$

$$Q^{(1,0)}\left[H\Omega - \Omega H_{eff}^{(1,0)}\right]p^{(1,0)} = 0 \tag{I.183}$$

All the quantities like wave function and effective Hamiltonian are η dependent. The Equations of (I.183) are η dependent and have to be solved for getting the cluster amplitudes and the effective Hamiltonian. Since effective Hamiltonian is complex, the model space coefficients along with the roots are also complex.

$$H_{eff}(\eta)C(\eta) = C(\eta)E(\eta) \tag{I.184}$$

To calculate resonance energy N electron ground state must be unperturbed. The $E(\eta)$ that we obtain from Equation (I.184) is not a good approximation to the resonance energy as N- electron state is also perturbation (η) dependent here. Thus, the more accurate way to get resonance energy is:

$$E_{res}(\eta) = E(\eta) + E_{srcc}(\eta) - E_{srcc}(\eta = 0) \quad \text{(I.185)}$$

In the CAP-FSMRCC methods CAP term is added at the SRCC level, making the procedure computationally expensive. To get-rid-of the problem, Sajeev *et al.* [31] proposed the CAP implementation within the CIP-FSMRCC approach of Bartlett and co-workers [323]. We approximate that:

$$T^{(0,0)}(\eta) = T^{(0,0)}(\eta = 0) \quad \text{(I.186)}$$

Using this we generate the $\bar{H}$ operator. Thus, in this approach we get rid of η dependence in the SRCC part. The correlated complex potential independent particle theory for resonance problem has the form:

$$\left(f + v_c(\eta)\right)\Phi_p = \varepsilon(\eta)\Phi_p(\eta) \quad \text{(I.187)}$$

Where f is the Fock operator, $v_c(\eta)$ is correlated complex potential. In order to get $v_c(\eta)$, we first solve FSMRCC equations without CAP. The first approximation to $v_c(\eta)$ is obtained by adding CAP potential to the one body part of $\bar{H}_N$. Iterative procedure is continued till the eigen values of $H_{eff}(\eta)$ are converged. Convergence is fast as we start from the converged cluster amplitudes which are independent of η as a first approximation.

I.14. Objective and scope of the thesis:

Before winding up the introduction part, we briefly mention the objective and scope and chapter orientation of the thesis.

In the thesis we have studied properties using energy or derivative of energy, and is done within FSMRCC frame work. The chapters are organized as follows:

First chapter: A general introduction is proposed leading to the subject matter of the thesis. Here, a brief overview of some of the basic concepts and developments in single reference coupled cluster theories are presented. Quasi-degenerate situations and their multi reference treatments are also highlighted. Introduction to computation of properties using numeric and analytic approach are discussed. We also introduce the idea of complex absorbing potential (CAP) and discuss the present status of CAPFSMRCC approach. We conclude the first chapter with the objectives and scope of the thesis.

Second chapter: The second chapter deals with shape resonance of electron-molecule collision. We present results of shape resonance arising from e^--F_2, N_2O and CO collision. We have used correlated independent particle Fock space multi reference coupled-cluster augmented with complex absorbing potential (CAP-CIP-FSMRCC).

Third Chapter: The optimization of geometry is an extremely important task in chemistry. It is indeed challenging to find the geometries of excited states. No results are available using the MRCC method, which can describe the excited states accurately. In this chapter, we have optimized the geometry of molecules within the FSMRCC framework using numerical gradients. Low lying excited states are dominated by single hole, single particle excitations from ground state closed shell molecules have been described in this chapter. Excited state gradients are done by calculation of using finite field multi reference coupled cluster method. We also report adiabatic excitation energies to confirm the excited state geometries. We report excited state geometries of CH^+, H_2O, O_3 and HCHO.

Fourth Chapter: Development of analytic gradients within the FSMRCC. This is the first attempts of implementing analytic gradients for FSMRCC. In this chapter we will give working equations for the analytic gradients of one valence problem.

Fifth Chapter: In this chapter we shall write general conclusion and scope of the thesis.

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CHAPTER II

Study of shape resonance: An application of Fock space multi-reference coupled cluster method

Abstract:

In this chapter we have applied correlated independent particle potential within Fock space multi-reference framework in augmentation with complex absorption potential , which has been developed by Sajeev *et al.* [Y. Sajeev, R. Santra, S. Pal, J. Chem. Phys. 123 (2005) 204110]. This is an advanced *ab initio* tool to calculate life time of resonances in the low-energy electron-molecule collision problem. This method quantitatively describes an elastic electron-molecule scattering below the first electronically inelastic threshold. The complex absorption potential is introduced for analytic continuation of the Hamiltonian to calculate position and width of resonance. In this method electron correlation, relaxation and analytic continuation are treated simultaneously. This method within Fock space multi reference formalism in augmentation with complex absorption potential is known as CAP-CIP-FSMRCC. In this chapter, we have studied shape resonance of e^-- F_2, e^--CO

and e^-- N_2O molecules. In particular, we have studied e^-- F_2 scattering at different bond lengths to know whether F_2^- is bound at the equilibrium bond length of F_2, and this molecule is important in several electrically excited gas lasers. Among the other three molecules N_2O, CO are of environmental interest.

II.1. Introduction:

Resonant states are metastable states, which are formed by temporary trapping of an electron in an atom or a molecule. The compound system has sufficient energy to break into neutral atoms or molecules and a free electron. Resonances are characterized by the complex energies called Siegert energy [1] associated with the eigen functions which diverge asymptotically. Unlike in bound state problem, where the wave function is square integrable and can be described by the basis set, resonance states are only quasi bound and are not square-integrable. Thus, it is desirable to transform the resonance problem into a bound state problem so that existing *ab initio* methods can be used for the calculation of resonance parameters. For past few decades efforts have been made to develop methods so that resonance energies can be calculated within the framework of *ab initio* bound state methods. Among these are the complex scaling [2-5], complex absorbing potential [6, 7] and stabilization methods [8-10]. All these methods use some parametrization in the Hamiltonian and several eigen values of the Hamiltonian are obtained as a function of this parameter. Empirical correlation methods are another way of studying the quasi bound states [11]. Complex scaling is also known as the complex coordinate method. In complex scaling method the information about the evolution of a resonance state at infinity is compressed into a small well defined space. Though conceptually simple, this method is complex to implement for molecules. Complex basis functions [12-14] are used to study the quasi bound states in molecules. Alternative approach is the use of complex absorbing potential (CAP). There are various attempts to construct an optimal absorbing potential [7, 15-18] for the calculation of resonance states. The popularity of the CAP approach is due to its simplicity in implementing with any electronic structure method. However, several states need to be studied at a time in order to identify the resonance state. Thus, methods which are suitable for studying multiple states at a time are useful. The idea behind the complex absorbing potentials is to introduce an absorbing boundary condition in the exterior region of the molecular scattering target which results in a non-Hermitian Hamiltonian. One of the square integrable eigen functions of this Hamiltonian corresponds to the resonance state. The associated complex eigen value then gives the position and width of the resonance. Since we use finite basis set it is difficult to separate the physical stabilization points from the nonphysical once. Sajeev and co-workers [19] have developed a new CAP scheme to eliminate the false resonance states from the real resonance states. CAP method has been successfully used for the study of vibrational quasi bound states [20, 21], *i.e.* Feshbach resonance. CAP has been successfully used for the study of shape resonance with multi-reference configuration interaction (MRCI) [22-25], Multi-reference coupled cluster (MRCC) [26, 27], Green's function [28-30], equation of motion-coupled-cluster (EOM-CC) [31] and the symmetry-adapted configuration interaction (SAC-CI) [32]. Position of the resonance state is energy difference of the N electron ground state and the electron attached (N+1) electron state. Fock space multi reference coupled cluster method (FSMRCC) [33-37] gives the direct difference energy and is successful for the accurate calculation of difference energies. In the CAP-FSMRCC method we apply the CAP potential in the single reference coupled cluster approach itself. In this approach electron correlation and the analytic continuation are treated simultaneously. We need to solve the SRCC and FSMRCC equations for each of the potential strengths in CAP-FSMRCC. Thus, it is computationally expensive. Bartlett and co-workers [38] formulated the correlated independent particle potential (CIP) within FSMRCC framework. In another approach we apply the CAP to CIP-FSMRCC method. We call this method as CAP-CIP-FSMRCC [39] to differentiate it from the CAP-FSMRCC method. At the converged limit both the methods should give the same results. CAP-CIP-FSMRCC method is computationally inexpensive and yet accurate. This method is tested for the study of the resonance of e^--molecule shape resonance [39, 40].

In this chapter we shall discuss on the shape resonance of e^-- F_2, e^-- CO and e^-- N_2O collision.

e^--F_2 scattering is an interesting system. The aim of this study is to see the effect of electron correlations on F_2 scattering. There are several theoretical studies [41-45] on electron F_2 scattering. Since the potential energy curves of the neutral ground state and the ionic ground state exhibit curve crossing. There is a controversy regarding the F_2^- being bound at the equilibrium bond length of the neutral F_2. The determination of the crossing point is important for the study of dynamics. The correct determination of the crossing point requires balance treatment of the electron correlation in the ionic as well as neutral state.

e^--CO scattering is interesting because it refers to a Π-resonance. Among different heteronuclear diatomic systems CO is an interesting system. We have studied e^--CO shape resonance.

Similarly, e^--N_2O scattering study is also an interesting system. There are significant discrepancies between the experimental [46-48] and theoretical results [49-51]. The controversy remains regarding existence of shape resonance of Σ symmetry. Experimental evidences showed that there are two distinct resonance peaks. The lower one is at 2 eV of Π symmetry, and higher at 8 eV of Σ symmetry.

The chapter is organized as follows. Section II.2 gives a brief review of the theoretical details of the method. In section II.3 deals with correlated complex potential and approximate form of correlated complex potential. Section II.4 gives results and discussion on them, followed by conclusions in section II.5.

II.2. Theoretical details:

In this section we briefly discuss the FSMRCC method with emphasis on correlated independent particle potential for resonance problem. In the next section we shall discuss in details about the method. The study of shape resonance involves temporary trapping of electron in the potential well created by the angular momentum barrier and the attractive forces at small distances. It is known that the method for studying resonance must be able to treat the electron correlation and continuum effects simultaneously. Also, it should be able to handle multiple states at a time. FSMRCC method provides direct difference energies of multiple states at a time and introduces electron correlation in an efficient manner.

In FSMRCC, N electron RHF is chosen as a vacuum, with respect to this vacuum holes and particles are defined. These are further divided into active and inactive space. The problem of our interest is one active particle which is a complete model space. The model space for the (1, 0) sector can be written as:

$$\Psi_{\mu}^{(0)(1,0)} = \sum_{i} C_{\mu i} \Phi_{i}^{(1,0)} \tag{II.1}$$

Where, $C_{\mu i}$'s are the model space coefficients and Φ_i's are the model space.

The correlated wave functions for the μ-th state is defined as:

$$\Psi_{\mu}^{(1,0)} = \Omega \Phi_{\mu}^{(0)(1,0)} \tag{II.2}$$

$$\Omega = \left\{ \exp(\tilde{T}^{(1,0)} + \tilde{T}^{(0,0)}) \right\} \tag{II.3}$$

Ω is the valence universal wave operator.

$T^{(1,0)}$ operator destroys exactly one active particle. The normal ordering of the operators prevents contraction between the T's. This leads to the decoupling of the equations for different Fock space sectors. The Bloch equation [52] for the $(1,\ 0)$ sector is:

$$P^{(1,0)}\left[H\Omega-\Omega H_{eff}\right]P^{(1,0)}=0 \qquad \text{(II.4)}$$

$$Q^{(1,0)}\left[H\Omega-\Omega H_{eff}\right]P^{(1,0)}=0 \qquad \text{(II.5)}$$

Equation (II.4) and Equation (II.5) define the effective Hamiltonian and amplitude equations.

P and Q are the model space and complementary space projection operators. FSMRCC method is discussed in chapter I. For even more details on FSMRCC see ref. [33].

In the CAP-FSMRCC approach for the resonance problem, electron absorption is achieved by adding the absorption potential to the Hamiltonian:

$$H(\eta)=H-i\eta W \qquad \text{(II.6)}$$

The strength of the potential is defined as η, W which is a local, non-negative semi definite one particle potential. In the limit that $\eta\to 0$, $H(\eta)$ describes the analytic continuation of the Hamiltonian H. All the quantities like wave function and effective Hamiltonian are η dependent. The Equation (II.4) and Equation (II.5) are η dependent and have to be solved for getting the cluster amplitudes and the effective Hamiltonian. Since effective Hamiltonian is complex, the model space coefficients along with the roots are also complex.

$$H_{eff}(\eta)C(\eta)=C(\eta)E(\eta) \qquad \text{(II.7)}$$

For the calculation of resonance energy N electron ground state must be unperturbed. The E (η) that we obtain from Equation (II.7) is not a good approximation to the resonance energy as N-electron state is also perturbation (η) dependent here. Thus, the more accurate way to get resonance energy is:

$$E_{res}(\eta) = E(\eta) + E_{srcc}(\eta) - E_{srcc}(\eta = 0) \qquad \text{(II.8)}$$

The CAP procedure described so far was implemented initially. However, it is computationally intensive as we need to calculate for each η the SRCC and FSMRCC equations. Since CAP is defined only over the particle-particle block, its effect on correlation energy is very small. Sajeev *et al.* [36] proposed the CAP implementation within the CIP-FSMRCC approach of Bartlett and co-workers [35]. Thus we approximate:

$$T^{(0,0)}(\eta) \sim T^{(0,0)}(\eta = 0) \qquad \text{(II.9)}$$

Using this, we generate the $\bar{H}$ operator. Thus, in this approach we get rid of η dependence in the SRCC part. The correlated complex potential independent particle theory for resonance problem has the form:

$$\left(f + v_c(\eta)\right)\Phi_p = \varepsilon(\eta)\Phi_p(\eta) \qquad \text{(II.10)}$$

Where f is the Fock operator, $v_c(\eta)$ is correlated complex potential. In order to get $v_c(\eta)$, we first solve FSMRCC equations without CAP. The first approximation to $v_c(\eta)$ is obtained by adding CAP potential to the one body part of $\bar{H}_N$. Iterative procedure is continued till the eigen values of $H_{eff}(\eta)$ are converged. Convergence is fast as we start from the converged cluster amplitudes which are independent of η as a first approximation. We have used

CAP-CIP-FSMRCC method truncated at singles doubles level (CAP-CIP-FSMRCCSD).

II.3. The Correlated Complex Potential:

The correlated complex potential $\tilde{V}_C(\eta)$ can be derived by incorporating a complex absorbing potential in the correlated potential. Correlated potential is introduced to solve Equation (II.10). Complex absorbing potential (CAP) is applied to render the wave function of the projectile square integrable, and leaving the target unaffected. To describe the (N±1)-electron state, the ground state with N-electronic configuration can be described by the Hamiltonian is unperturbed by CAP. In order for the CIP method to have a CAP unperturbed target state, we eliminate the effect of the CAP on the Hartree-Fock ground state by replacing

$$W \rightarrow PWP \tag{II.11}$$

Where, P is the projection operator, which projects onto the subspace of unoccupied orbitals and is defined as:

$$P = \sum_i |\phi_i\rangle\langle\phi_i| \tag{II.12}$$

Rewriting W as:

$$\langle\phi_p|W|\phi_q\rangle = 0 \tag{II.13}$$

Between p and q, if anyone is an occupied orbital, then the cluster amplitudes of the (0,0)-sector, *i.e.*, in the single reference case is invariables with respect to the CAP and can be expressed as:

$$t^{(0,0)}(\eta) = t^{(0,0)}(\eta = 0) \qquad \text{(II.14)}$$

Since we have to study electron attachment, so here we shall focus on correlated complex potential for electron attachment phenomena ((N+1) electronic state), *i.e*. (1, 0) sector of the Fock space and we introduce CAP potential into FSMRCC theory. To introduce it in both the (0, 0) and (1, 0) sectors to completely define the valance universal wave operator for the CAP perturbed Hamiltonian.

$$H(\eta) = H - i\eta W \qquad \text{(II.6)}$$

Due to subsystem embedding condition (SEC) to solve the cluster amplitudes, the first step would be to introduce CAP one-body term in the single reference case, *i.e.*, (0, 0) sector of the Fock space. The physical concepts make it possible to apply the perturbation by CAP directly to the next hierarchical sector of Fock space defined by SES. Within FSMRCC framework the only one-body interaction terms of $\bar{H}_N$. Similarly to the $\bar{H}_N$ interaction, in order to introduce the CAP perturbation in the (1, 0) sector of Fock space, the CAP perturbation term can be transformed into $\bar{W}_N$ interaction term:

$$\bar{W}_N(\eta) = \left[-i\eta W_N \exp\left(T^{(0,0)}\right)\right]_{connected,open} \qquad \text{(II.15)}$$

The CAP interaction term satisfies (II.13) and $\bar{W}_N$ is defined by (II.6). The idea of analytic continuation for the effective Hamiltonian is to replace all the one-body particle-particle interactions of $\bar{H}_N$ diagrams entering $V_C^{(1,0)}$ and $T^{(1,0)}$ amplitudes with a new particle-particle interaction of the form:

$$\left(\bar{H}_N(\eta)\right)_{one-body} = \left(\bar{H}_N\right)_{one-body} + \bar{W}_N(\eta) \qquad \text{(II.16)}$$

In FSMRCC method, the new set of non-linear $T^{(1,0)}(\eta)$ amplitude equations are solved by iterative manner, and the solution of the new effective Hamiltonian is:

$$\bar{H}_{eff}^{(1,0)}(\eta)C_{pp}^{(1,0)}(\eta)=\left(\varepsilon_{HF}^{EA}+V_{C}^{(1,0)}(\eta)\right)C_{pp}^{(1,0)}(\eta)=C_{pp}^{(1,0)}(\eta)\varepsilon_{P}^{(1,0)}(\eta) \qquad \text{(II.17)}$$

and is equivalent to Bloch equation:

$$P^{(1,0)}H(\eta)_{N}\,\Omega(\eta)P^{(1,0)}=P^{(1,0)}\Omega(\eta)H(\eta)_{N,eff}\,P^{(1,0)} \qquad \text{(II.18)}$$

$H(\eta)_N$ is the normal ordered form of the Hamiltonian $H(\eta)$ of Equation (II.6). $\varepsilon_P^{(1,0)}$ is the solution Equation (II.17) and are the correlated complex of EAs of $H(\eta)$. In a similar fashion the correlated complex potential for ionization, *i.e.*, can be calculated by replacing the particle-particle one body part of the $\bar{H}_N$ interactions in $V_C^{(0,1)}$ and $T^{(0,1)}$ with the particle-particle $\bar{H}_N$.

II.3.A. Approximated form of correlated complex potential:

The analytic continuation method computationally easier. Theoretical methods treat the full scattering problem including non-resonant contribution to the scattering cross section [53-56], but there are difficulties in computing resonance parameters using analytic continuation methods. These are:

1) Since the finite basis set is used, thus it is difficult to locate which complex eigen value in the discrete spectrum may correspond to resonant state. For a complete basis set, for every resonance state, there exists an eigen value $E(\eta)$ of $H(\eta)$, which satisfies

$$\lim_{\eta \to 0^+} E(\eta) = E_r - i\frac{\Gamma}{2} \qquad \text{(II.19)}$$

On the other hand in the approximate numerical treatments using a finite basis set, the resonance energy shows certain stability properties, and in practice they are determined form 'stabilization graphs', because the complex velocity, $v_i(\eta)(v_i(\eta) = \eta\frac{\partial E_i}{\partial \eta})$ of one of the trajectories is minimum in magnitude near the resonance energy [57, 58]. Graphical optimization by analytic continuation parameters is time consuming and not worthy in terms of computation, because the electronic structure calculation must be performed several times using a large basis set.

2) Electron correlation and relaxation effects are important in locating the position and width of resonances. In *ab initio* methods, where the analytic continuation scheme has been framed should describe correlation energy accurately. The accurate calculation of resonance parameters requires heavy computational expenses due to the stabilization graphs and they are equivalent of electron correlation. The difficulty of the stabilization method is again increased by optimizing the geometric parameters which minimizes CAP perturbation and maximizes the electron-overlap with the wave function of the scattered electron.

To get CIP potential, first we have to solve the non-linear FSMRCC equations. The expression for the first iterative solution of the $V_C^{(1,0)}(\eta)$ problem can be obtained from the unperturbed $V_C^{(1,0)}$, by replacing the one-body part of the $\bar{H}_N$ interactions with the CAP augmented one-body part of the Hamiltonian interactions $\bar{H}_N(\eta)$ (Equation (II.16)). In fig. II.1(a) we have shown the resultant $V_C^{(1,0)}$, which is represented as $V_C^{(1,0)}(\eta)$. $V_C^{(1,0)}(\eta)$ is coupled with $\bar{H}_N(\eta)$ interactions from (II.18) generates $T^{(1,0)}(\eta)$ diagrams (fig. II.1(b)), the CAP unperturbed $V_C^{(1,0)}$ contribution from $T^{(1,0)}(\eta)$ is dropped and substituted it with the $V_C^{(1,0)}(\eta)$ diagrams. This CAP contribution can be written in term of $\bar{H}_N(\eta)$ and the CAP unperturbed amplitudes are within parentheses of fig. II.1 (c). Following the iterative procedure, using new cluster amplitudes, correlated potential can be generated for next iteration. This iteration can be continued until the eigen values of $\bar{H}_{N,eff}(\eta)$ converges.

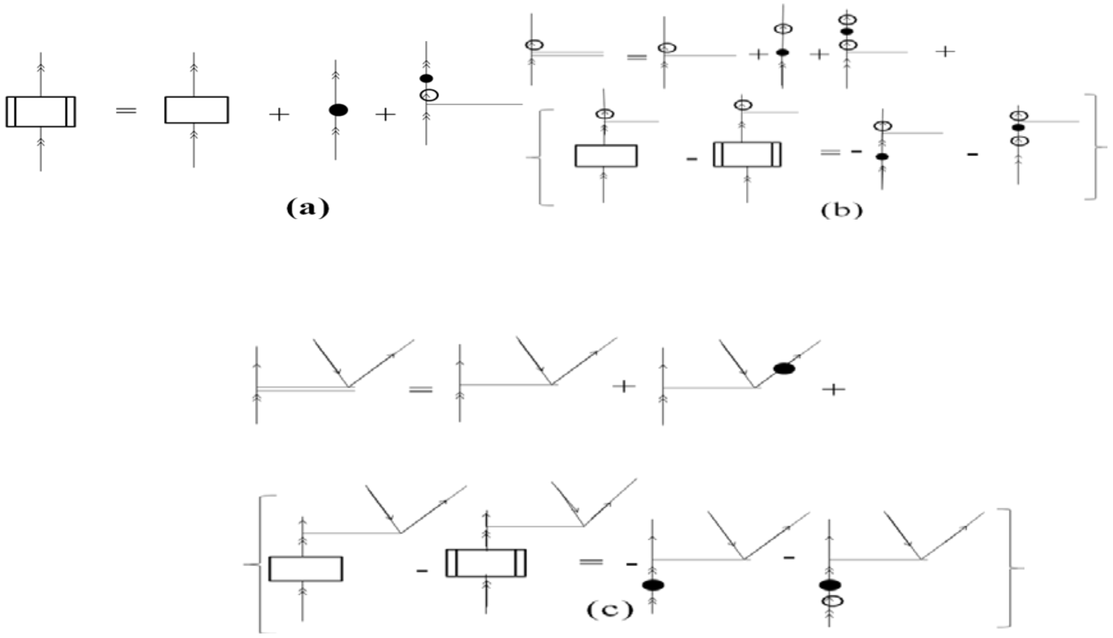

fig. II.1 The CAP perturbed FSMRCC diagrams. (a) $V_c^{(1,0)}(\eta)$, (b) $T_1^{(1,0)}(\eta)$, (c) $T_2^{(1,0)}(\eta)$ diagrams. $\bar{W}$ perturbation is denoted by filled circles, vertical double lines indicate CAP-perturbed excitations and the CAP-perturbed correlated potential is symbolized by box with vertical lines.

The CAP-FSMRCC and CAP-CIP-FSMRCC are theoretically equivalent in defining the analytic continuation of the Hamiltonian, but they differ in the implementation. In CAP-FSMRCC the analytic continuation starts from many-body Hamiltonian and the diagonalization of the complex effective Hamiltonian gives the resonance energy, relative to the target state. On the other hand in CIP-CAP-FSMRCC the analytic continuation scheme starts from the real FSMRCC effective Hamiltonian and the diagonalization of the iteratively solved new complex effective Hamiltonian yields an equivalent energy difference.

From the above discussion we can say that using CAP-CIP-FSMRCC studying the resonance trajectory becomes simplified, when the iterations are terminated after correlated potential calculation. This truncation of the iterative procedure is justified by the fact that the H_{eff} and $T^{(1,0)}$ amplitudes are converged quantities for the CAP unperturbed H_{eff} and eigen values of H_{eff} corresponds to the correlated electronic states of the (N+1) -electron system. The dynamic and non-dynamic correlation for (N+1) -electron states are retained in this procedure. A suitably chosen CAP should define an exact analytic continuation for the Fock space $(1,0)$ sector with a minimum change in the correlation energy. Termination of the iterative procedure in the second step of the complex correlated potential calculation is advantageous over the CAP-FSMRCC procedure is that:

1) No modified calculation of the FSMRCC is required for bound states, minimum changes in the cluster amplitudes of (1, 0)-sector and $\bar{H}_{N,eff}$ matrix.

2) Construction of $T^{(1,0)}$ is the most expensive part of FSMRCC calculation. In this case, once $T^{(1,0)}$ matrix generated can be used for $T^{(1,0)}(\eta)$ and $T^{(1,0)}(\eta^1)$ can easily be constructed from $T^{(1,0)}$, just by adding a few diagrams. Whereas, in CAP-FSMRCC for each η value, this step has to repeat.

II.4. Results and discussion:

We have used CAP-CIP-FSMRCCSD for the study of e^--F_2, CO and N_2O resonance study. For our study of resonance we chose box shaped CAP, which is applied in the peripheral region of the box leaving target unperturbed. The form of the potential is:

$$W(x;C) = \sum_{i=1}^{3} W_i(x_i;C_i) \qquad \text{(II.20)}$$

$$W_i(x_i;C_i) = \begin{cases} 0 & |x_i| \le C_i \\ \\ (|x_i| - C_i)^2 & |x_i| > C_i \end{cases} \qquad \text{(II.21)}$$

The CAP box size is such that:

$$C_x = C_y = \delta C$$

$$C_z = R/2 + \delta C$$

II.4.A. Fluorine:

Fluorine is a closed-shell molecule with a ${}^2\Sigma_u^+$ ground state. Molecular fluorine is an important constituent in several electrically excited gas lasers, *e.g.*, for rare-gas-fluoride laser modeling. The electron scattering of fluorine molecule has been investigated theoretically several times. The theoretical treatment of e^--F_2 scattering is complicated due to strong polarization of the target. It is expected that the correlation as well as polarization will play an important role in the accurate description of the resonance, in particular for highly electronegative molecule like, fluorine.

The R-matrix study by Morgan *et al*. [43] used static exchange model with polarization (SEP). Their study found that the ionic state is stable against auto-detachment at the equilibrium internuclear separation of the neutral molecule. The R-matrix calculations at the SEP level of correlation indicates that the position of the crossing point of the ionic and neutral potential curve is strongly influenced by the correlation included in the fixed-nuclei calculation. The resonance structure becomes narrower as R approaches the crossing point of the potential curve of neutral molecular ground state with the negative ion. It was predicted that the resonance could be an artifact of the static exchange approximation and would disappear if correlation effects were included.

We have used d-aug-cc-pVDZ basis set [59] in our calculation. The electronic configuration of F_2 in its ground state is:

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^4$$

We have studied resonance of F_2^- at various bond lengths, *viz*., 2.47, 2.57, 2.62, 2.64 and 2.67 a.u., respectively.

In TABLE II.1 we report the crossing point where the resonance turns into the bound state for different theoretical methods. In our study we find that at 2.67 a.u., *i.e*., the equilibrium bond length of neutral F_2, the electron affinity of F_2 is positive, indicating that F_2^- is becoming bound at this geometry. Ingr *et al*. [44] calculated the crossing point of the neutral target potential curve with the resonance state potential curve by the extrapolation of the resonance width to zero. Ingr *et al*. [44] used CAP-MRCI method to find out the crossing point of the two curves. They obtained 2.623 a.u. as the point where F_2^- is stable. Later Brems *et al*. [42] used Feshbach-Fano R matrix method to find the crossing point. Though the basis set used is same and the crossing point was at 2.41 a.u. The SD-MRCI results of Tarana *et al*. [45], found that F_2^- becomes bound at 2.76 a.u. which is quite high compared to all other theoretical calculations. The basis set used by Tarana *et al.* [45], is cc-pVTZ for F atom while the continuum basis is same as that of Brems *et al*. [42] Tarana *et al*. [45], studied three different models, static exchange (SE), static exchange-plus-polarization (SEP) and single and double excitations multi-reference CI (SD-MRCI). Their study at the SE level shows resonance for the equilibrium internuclear distance which vanishes at the SEP level. SD-MRCI method resonance is observed, however position and width are different. Thus, it can be inferred that the position of the crossing point of the neutral target potential curve with the ionic potential is sensitive to the inclusion of electron correlation. Though, basis set as well as methods used are widely different, it can be seen that all the MR methods are having qualitatively similar value of the crossing point. Here, we would like to mention that in FSMRCC method the electron correlation is consistently included in the neutral as well as ionic state giving more balanced treatment of electron correlation. Whereas, in

MRCI treatment of electron correlation is unbalanced because of the independent calculations for the ionic and neutral target states. Since the position of the resonance is difference of (N+1) and N electron state, *i.e.*, electron affinity. We have also checked the electron affinity of the fluorine atom. We obtain 3.21 eV compared to the 2.2 eV of SD-MRCI of Tarana *et. al.* [45], 13.5 eV using SEP by Brems *et al.* [42] and 3.54 eV using MRCISD (MRCI method truncated at singles doubles level) by Ingr *et al.* [44]. The experimental electron affinity is 3.4 eV. It is interesting to note that FSMRCCSD and MRCISD results are closer to the experimental value compared to the other theoretical method. Also these two methods give crossing points as 2.67 eV and 2.62 eV, which are quite well in agreement with each other despite of different basis sets.

We report the resonance energy and width at different bond lengths in TABLE II.2. Using CAP-CIP-FSMRCCSD and CAP-MRCISD results of Ingr *et al.* [43], for bond lengths where ever results are available. Ingr *et. al*. [43], have used [5s4p2d1f] basis, the continuum part of the wave function is described using diffuse s and p functions which is different for different bond lengths. Though basis sets are widely different. We still report them to have qualitative comparison. From TABLE II.2 we can see that with the bond distance width of resonance decreases sharply in both the methods, implying more lifetimes of the meta-stable state. It can be seen that the width of resonance is much more sensitive to the basis set than the position. At the equilibrium distance of neutral F_2, F_2^- is bound.

TABLE II.1. Bond lengths in a.u. where the resonance state turns into the bound state:

R	Method	Basis
2.41[a]	Feshbach-Fano partitioning method (FFR)	5s4p2d1f
2.56[b]	R-matrix method	----
2.62[c]	CAP-MRCISD	5s4p2d1f+continuum basis
2.76[d]	SD-MRCI	cc-pVTZ+continuum basis
2.67	CAP-CIP-FSMRCCSD	d-aug-cc-pVDZ

a: Ref. 42.

b: Ref. 43.

c: Ref. 44.

d: Ref. 45.

TABLE II.2. Position and width of shape resonance for e^--F_2 for various bond lengths:

Bond length (a.u.)	**Energy (eV)**	**Width (eV)**	**Energy (eV)**	**Width (eV)**
	CAP-MRCISD		**CAP-CIP-FSMRCCSD**	
2.47	1.726	0.021	1.178	0.147
2.57	0.576	0.0029	0.582	0.082
2.62	------	------	0.220	0.060
2.64	------	------	0.065	0.048

II.4.B. Carbon monoxide:

The electronic molecular orbital configuration of CO is:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$$

We report the $^2\Pi$ resonance which is obtained by adding an electron in the $^2\Pi$ state of the ground state of CO. We have used 4s4p basis for carbon and oxygen used by Mishra *et al.* [60-62]. We compare our results with other theoretical and experimental results [63]. All the values are reported in TABLE II.3. For CAP-CIP-FSMRCCSD calculations the CAP box lengths chosen were $C_x = C_y = \delta C$ and $C_z = 1.068 + \delta C$, where, C_x, C_y, C_z are distances from centre of the coordinate system along the x, y and z-axis, respectively and δC =10 a.u. CAP-CIP-FSMRCCCSD predicts resonance at 1.19 eV with the width of 0.07

eV. The second order dilated electron propagator [61] and bi-orthogonal [62] electron propagator in the same basis predict position of 1.71 and 1.68 eV, respectively. Our results underestimate the resonance position. However, our width is in good agreement with the width obtained using propagator method which is in the same basis. Compared to the experimental values our position and width are quite small due to basis set.

TABLE II.3. Resonance Energy and width of the e^--CO shape resonance:

Method	**Energy (eV)**	**Width (eV)**
Experiment[a]	1.50	0.40
Boomerang Model[b]	1.52	0.80
Close coupling[c]	1.75	0.28
Second order dialated propagator[d]	1.71	0.08
Bi-orthogonal propagator second order[e]	1.68	0.09
CAP-CIP-FSMRCCSD	1.19	0.07

a: See ref. 62.

b: See ref. 63.

c: See ref. 64.

d: See ref. 61.

e: See ref. 60.

To study the basis set effects and convergence with the basis set, we have studied CO in maug-cc-pVDZ basis and added p function on C and O. The p-functions were obtained by scaling the previous p coefficient by 0.75. The results are reported in TABLE II.4. It can be seen that the width is very sensitive to the basis set. With addition of each p functions width and positions of resonance is reduced. The width is converged to 0.32 eV after addition of 4p functions. The position of the resonance is at 1.22 eV compared to experimental value, position and width are still small. However, it has approached the experimental value compared to the 4s5p basis

TABLE II.4. Basis set convergence for CO:

Basis set	**Position (eV)**	**Width (eV)**
Experiment[a]	1.50	0.40
Maug-cc-pVDZ	3.02	0.46
Maug-cc-pVDZ+1p (C 1p/O 1p)	2.15	0.35
Maug-cc-pVDZ+2p (C 2p/O 2p)	1.68	0.32
Maug-cc-pVDZ+3p (C 3p/O 3p)	1.19	0.31
Maug-cc-pVDZ+4p (C 4p/O 4p)	1.22	0.32

a: See ref. 62.

II.4.D. Nitrous oxide:

N_2O is present in the upper atmosphere which plays an important role in depletion of ozone layer [65]. We have chosen d-aug-cc-pVDZ basis set [59].

The N-N and N-O bond lengths are 2.13 and 2.24 a.u., respectively. Electronic configuration of N_2O in its ground state is:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 7\sigma^2 2\pi^4$$

There have been several experimental [46-48] and theoretical [49-51] studies for N_2O resonance. Two shape resonances have been reported one at 2.2 eV and the other one at 8 eV. TABLE II.5 reports the resonance energy and width for Σ and Π states using different methods. Morgan *et al.* [50] did static exchange (SE) and static-exchange-plus-polarization (SEP) model calculations for N_2O. The SE results of Morgan *et al.* [50], were similar to the one obtained by Sarpal *et al.* [49] They found the low energy $^2\Pi$ resonance, however, they did not find a $^2\Sigma$ resonance below 10 eV in either model. The SEP calculations predict $^2\Pi$ resonance peak at 1.99 eV with a width of 0.35 eV. In our study the lower resonance, i.e., $^2\Pi$-resonance energy is at 2.34 eV with the width of 0.34 eV. Our resonance energy matches well with the experimental values. However, experimental width is available only for impulse approximation which is quite high compared to all the theoretical results. Using impulse approximation Dubé [48] showed the position and width of resonance at 2.3 eV and 0.7 eV, respectively. The width of the resonance is less using CAP-CIP-FSMRCCSD compared to the CI [49] and Schwinger Multichannel method [51]. Coming to the $^2\Sigma$ resonance we find that CAP-CIP-FSMRCCSD gives position at 7.77eV with the width of 1.64 eV. Our results for position and width are slightly less compared to the other theoretical and experimental values. Sarpal *et al.* [49] obtained position and width at 8eV and 2 eV, respectively.

Schwinger multichannel method [48] gives position at 8 eV with the width of 2.8 eV. Vibrational excitation measurement of Andrić and Hall [46] showed a resonance peak at 8.3 eV with the width slightly greater than 3 eV.

TABLE II.5. Resonance Energy and width of the e^-- N_2O shape resonance:

State	Method	Energy (eV)	Width (eV)
$^2\Pi$	Linear transmission experiment[a]	2.25	-----
	Impulse approximation[b]	2.30	0.70
	Vibrational Excitation[c]	2.30	-----
	Configuration interaction[d]	2.15	0.64+0.1
	Static Exchange Polarization[e]	1.99	0.35
	Schwinger multichannel[f]	2.19	0.52
	CAP-CIP-FSMRCCSD[g]	2.34	0.34
$^2\Sigma$	Vibrational Excitation	8.30	3.00
	Configuration Interaction	8.00	2.0
	Schwinger multichannel	8.00	2.80
	CAP-CIP-FSMRCCSD	7.77	1.64

a: see ref. 47.

b: see ref. 48.

c: see ref. 46.

d: see ref. 49. 5s3p1d+continuum basis

e: see ref. 50. 5s3p1d $\alpha_d = 1.8846$

f. See ref. 51. 6-31+ (2d)

g. d-aug-cc-pVDZ.

II.5. Conclusion:

In this chapter we have used CAP-CIP-FSMRCCSD method to study the resonance position and width of e^--F_2, e^-- CO and e^-- N_2O shape resonance. For study of shape resonce we have used d-aug-cc-pVDZ basis set is used for F, N and O for e^--F_2 and e^--N_2O shape resonance study.

For F_2 we have studied the resonance at different bond lengths of F_2, starting from 2.47 to 2.67 a.u. It has been observed that with the bond length resonance position and width drops. At the equilibrium bond length of F_2 *i.e.*, 2.67 a.u., electron affinity becomes positive, indicating that F_2^- becomes stable and no resonance is observed. We report in TABLE II.1 results of various previous studies indicating bond length of F_2 at which F_2^- is bound. Our results are in good agreement with the previous CAP-MRCISD results of Ingr *et. al.*

For CO we have used 4s5p basis used by Mishra *et al.* for comparison. CAP-CIP-FSMRCCSD underestimates the position of resonance. However, our width (0.07 eV) is in good agreement with the second order peopagator (0.08 eV) and biorthogonal propagator (0.09 eV). Basis set convergence studies have been done by adding evenly tempered p functions to the maug-cc-pVDZ basis. It has been observed that upon addition of each p function, both resonance position and width is reduced, finally width is converged to 0.32 eV after addition of 4p functions. This study shows the importance of basis set for the study of shape resonance.

N_2O is another system we have studied. Experimental results confirm double resonance with lower one positioned at 2 eV corresponds to Π-symmetry and higher of Σ-symmetry. We get ${}^2\Pi$ resonance at 2.31 eV and ${}^2\Sigma$ at 7.77 eV. Our results are in good agreement with the experimental results.

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CHAPTER III

Excited state geometry optimization by using Fock-space multi-reference coupled cluster method

Abstract:

The Fock space multi-reference coupled-cluster (FSMRCC) method is used for the geometry optimization of the low-lying excited states of the molecules. Molecular geometries of the carbon monohydride cation (CH^+), water (H_2O), ozone (O_3) and formaldehyde (HCHO) in their low lying excited states are optimized. Excited state gradients are calculated using finite field multi reference coupled cluster method. We also report the adiabatic excitation energies in order to examine the nature of stationary point obtained via geometry optimization. We compare our results with other theoretical and/or experimental results.

III.1. Introduction:

Single reference coupled cluster (SRCC) [1-4] method is very successful in describing energy and properties of closed shell and high spin open shell molecules [5-9]. The underlying assumption in SRCC is that the wave function is dominated by a single determinant. However, this assumption no longer works for excited states, bond dissociation, transition states and various other problems. To handle these situations within single reference framework, various methods exsists in the literature, like active space CC [10], method of moments approach (MMCC) [11], tailored CC (TCCSD) [12, 13], Equation-of-motion CC (EOM-CC) [14-16], renormalized CC methods [17]. However, a more general solution is to use genuine multi reference methods.

Multi reference coupled cluster (MRCC) methods incorporate non dynamic electron correlation in an effective manner. There are two subclasses of MRCC methods, which have been studied extensively. One is the multi root description via effective Hamiltonian approach [18-20] and the other describes a specific root, known as the state-specific (SS) MRCC [21] approach. Methods based on the effective Hamiltonian approach are further divided into the Hilbert space (HS) [22-25] and Fock space (FS) [26-31] approach depending on the way the dynamic part of electron correlation is described. Both these approaches are fully size-extensive. In both the approaches energies of the states are obtained by diagonalization of the effective Hamiltonian defined within a pre-chosen model space. The Fock-space multi-reference coupled cluster (FSMRCC) method has been used successfully for energies of excited states [32], ionized states [33] and electron attached states. FSMRCC is known to describe the quasi-degeneracy of the low-lying states of the above types quite efficiently. FSMRCC method uses valence universal wave operator, which correlates the model spaces with the exact wave function. The Hilbert space approach uses a state-universal wave operator with different cluster operators for each determinant in the model space. The method has been used for studying potential energy surface (PES), bond-dissociation [34], etc. FSMRCC as well as HSMRCC suffer from the convergence problem due to the presence of the intruder states. To eliminate the intruder state problem Intermediate Hamiltonian (IH) theory [35] can be used. The other solution to avoid intruder state problem is to use state-specific (SS) MRCC [36, 37] approach. However, there is no unique way to define state specific MRCC approach. Among few are Brillouin-Wigner (BW) MRCC ansatz [38], exponential multi-reference wave function ansatz (MRexpT) [39], the state-specific MRCC method suggested by Mukherjee and coworkers (Mk-MRCC) [40] and Internally contracted multi-reference coupled cluster (ic- MRCC) [41] theory. However, for PES, the state selective MRCC method developed by Mukherjee and co-workers [40] is found to be more suitable in recent years from the point of view of circumventing the important problem of intruder states. Parallel to this, methods like equation-of-motion coupled cluster (EOM-CC) [14-16], symmetry-adapted cluster configuration interaction [42, 43], similarity transformed EOMCC (STEOM-CC) [44] approaches have been developed to handle cases of quasi-degeneracy.

There are attempts of inclusion of full or partial triples within FSMRCC [45-48] framework. Pal and coworkers implemented partial triples for ionization potential [46] and excitation energies [46]. Bartlett and coworkers

[48] have included full triples corrections for the excitation energies within intermediate Hamiltonian based FSMRCC. Inclusion of iterative and non-iterative triples within EOM-CC [49-50] and state selective [51] approaches for energy calculation has also been done. Piecuch *et al*. [52] implemented the non-iterative corrections to method of moments coupled cluster (MMCC) for excitation energies.

Analytic formulation of the energy gradients began with the pioneering work of Pulay [53]. While analytic derivative formalism [5] of single reference coupled cluster (SRCC) method [1-4] is well studied, a similar formalism for multiple root problems is very recent. Accurate calculations of energy derivatives with respect to different perturbations are important for problems of chemical interest. Energy derivative with respect to displacement of the nuclei is one of the key ingredients in describing the effect of molecular vibrations on properties computed within the Born-Oppenheimer approximation. The energy derivative with respect to coordinates are necessary to find out the stationary point on the potential energy surface [9, 54]. Spectroscopic constants like infra-red [55, 56] and Raman [56-59] properties are important in the determination of molecular structure.

First order properties can be obtained using expectation value or response approach. For approximate methods these two approaches do not lead to same results. Analytic derivative or what is known as a response approach is preferred in particular for CC because the expectation value approach does not truncate naturally. Along the line of the SRCC linear response approach [5], MRCC analytic linear response approach was developed by Pal [60] and then implemented by Ajitha *et al*. [61, 62] for dipole moment of the doublet radicals. However, this initial approach is unsatisfactory, since it requires cluster amplitude derivatives for first energy derivatives. To eliminate the amplitude response dependence a method called Z-vector method [63] was first used in configuration interaction. Later, this technique was also used for EOM-CCSD [64], SAC-CI [65] and SRCC [66] gradients. Taking clue from the developments in SRCC context, the constrained variation formulation [67] using Lagrange multiplier was developed by Pal and co-workers [68, 69] for Fock as well as Hilbert space. This approach has been tested well for the electric [70, 71] and magnetic properties [72]. Szalay [73] independently developed response approach formulation based on Lagrange multipliers for compete model spaces. Lagrange multiplier approach has been applied for CI [74], MBPT [75], EOM-CC [75], STEOM-CC [76] and Mk-MRCC [77] methods to get analytic gradients.

FSMRCC and EOM-CC are equivalent for one valence problem. However, this equivalence breaks down for higher sectors. However, no study of excited state FSMRCC gradients is currently available. Analytic evaluation of excited state gradients within FSMRCC framework requires considerable computational effort. The coupled perturbed orbital contribution needs to be evaluated for each sector of the Fock space. As an initial application in this paper, we have used numerical approach for the calculation of the gradient of the excited state dominated by the HOMO to LUMO excitation. Using numerical gradients we have optimized the excited state geometries. The calculated gradients have been validated by calculations of adiabatic excitation energies and compared with the corresponding experimental or available theoretical results.

This chapter is organized as follows: In section III.2 we give a brief theoretical background of the method. Results and Discussion on them are presented in section III.3, using low lying excited states of CH^+, H_2O, O_3 and HCHO as test cases. Section III.4 gives conclusions on them.

III.2. Theoretical background:

Fock space multi-reference coupled cluster (FSMRCC) method is based on the concept of a common vacuum. An N-electron RHF configuration is chosen as a vacuum, with respect to which holes and particles are defined which are further divided into active and inactive holes and particles. We briefly introduce the notations to be used in this paper. The model space determinants with 'h' active holes and 'p' active particles are denoted as $\Phi_i^{(p,h)}$. Thus, the starting multi-reference wave function for a $(\mathrm{p},\,\mathrm{h})$-valence Fock space can be written as:

$$\left|\Psi_\mu^{(0)(p,h)}\right\rangle = \sum_i C_{\mu i}^{(p,h)} \left|\Phi_i^{(p,h)}\right\rangle \qquad \text{(III.1)}$$

Where, C's are the model space coefficients for the model space $\Phi_i^{(p,h)}$ with p active particles and h active holes. The correlated wave function is written as:

$$\Psi_\mu^{(p,h)} = \Omega \Psi_\mu^{(0)(p,h)} \qquad \text{(III.2)}$$

Where a wave operator Ω can be written as:

$$\Omega = \left\{ \exp\left(\tilde{T}^{(p,h)} \right) \right\} \tag{III.3}$$

Curly bracket denotes normal ordering of the operators in it. To generate the exact states for the $(\mathrm{p},\ \mathrm{h})$-valence system, the wave operator must generate all valid excitations from the model space. Normal ordering ensures that the contractions among different cluster operators within the exponential are avoided, leading to a hierarchical decoupling of the cluster equations. This is commonly referred to as a sub-system embedding condition (SEC) [78]. The Fock space Bloch equation [79] is solved using SEC *i.e.*, starting from $(0,0)$ sector to desired Fock space sector. The Projection operator P is defined as:

$$P = \sum_i \left| \Phi_i^{(p,h)} \right\rangle \left\langle \Phi_i^{(p,h)} \right| \tag{III.4}$$

and the orthogonal operator Q is defined as $1-P$. The Bloch equation has a form:

$$P^{(k,l)} \left[H\Omega - \Omega H_{eff} \right] = 0$$

$$\forall k = 0,1; \;\; l = 0,1 \tag{III.5}$$

$$Q^{(k,l)} \left[H\Omega - \Omega H_{eff} \right] P^{(k,l)} = 0$$

$$\forall k = 0,1; \;\; l = 0,1 \tag{III.6}$$

The model space for the low lying excited states can be described by a one hole-one particle state, and is denoted as $(1,1)$ sector of the Fock space. In the case of complete model space (CMS), the intermediate normalization is commonly employed. However, for incomplete model space (IMS), intermediate normalization has to be abandoned. It is shown by Pal *et al.* [32] that since $(1,1)$ sector is a quasi-complete model space, intermediate normalization can be used without any loss of generality. The lower valence cluster equations are completely decoupled from the higher valence cluster amplitude equations because of the SEC. Thus, the Bloch equations are solved progressively from the lowest valence $(0,0)$ sector upwards to $(1,1)$ valence sector. Lower valence amplitudes, once solved, appear as constants in the equation for the higher valence amplitudes. The effective Hamiltonian is constructed for $(1,1)$ sector and spin adapted for the singlet and triplet states. The energies of the corresponding sates are obtained by diagonalization of the spin-adapted effective Hamiltonian within the model space.

$$H_{eff}^{(1,1)}C^{(1,1)} = EC^{(1,1)} \tag{III.7}$$

To optimize the geometry of the singlet and triplet states, we have used FSMRCC method using singles and doubles truncation scheme (FSMRCCSD). Gradients are obtained by numerical differentiation of energy. Molecular symmetry has been used to decrease the computational effort. In the calculation of geometry optimization, a cut off of 10^{-4} has been taken on root mean square (RMS) gradient.

To verify the geometry obtained from the above procedure, we have calculated the adiabatic excitation energy of the molecule corresponding to that state and compared it with the experimental or available theoretical adiabatic excitation energy. This also validates the optimized geometry of the excited state. To obtain the adiabatic excitation energy, we start with the optimized geometry through the excited state geometry gradients obtained numerically. The RHF at this geometry is chosen as a vacuum. The Bloch equation is solved up to the $(1,1)$ sector using SEC. We retain the closed part of $\bar{H}$ explicitly and hence, we obtain the total energy of the corresponding excited state. Finally, to obtain adiabatic excitation energy, we subtract from this only the closed part of $\bar{H}$ at the ground state geometry.

III.3. Results are discussion:

Fock space multi-reference coupled cluster is used for the geometry optimization of low-lying excited states. We have chosen carbon mono-hydride cation, water, ozone and formaldehyde as test systems for our study. Along with the excited state geometries, we also report adiabatic excitation energies for all the molecules. We report the singlet and triplet geometries of the excited states dominated by the homo-lumo excitation. We compare our results with the EOM-CCSD, coupled cluster linear response theory (CC-LRT), Full CI (FCI) and experimental results where ever available. EOM-CCSD results obtained using ACES II [80]. CC-LRT calculations were done using MRCC [81] where as FCI calculations were done using GAMESS software [82]. For formaldehyde we compare our results with MRCISD and MRAQCC method [83].

III.3.A. Carbon monohydride cation (CH^+):

CH^+ is a 6 electron system with the MO configuration of, $1\sigma^2 2\sigma^2 3\sigma^2$. RHF of CH^+ is chosen as a vacuum. A large non-dynamic electron correlation contribution comes from the $1\sigma^2 2\sigma^2 1\pi^2$ configuration. We report the excited state geometry of the singlet and triplet Π state dominated by the HOMO to LUMO excitation, *i.e.*, from $3\sigma_g \rightarrow 1\pi_u$. Model space consists of one active hole and two active particles. We have used three different basis sets in our study. cc-pVDZ, cc-pVTZ [84] are the two basis sets. Third basis consists of Dunning double zeta plus polarization basis [85] augmented with diffuse s and p functions on carbon and one diffuse s function on hydrogen. The final basis set is (10s6p1d)/[5s3p1d] for carbon and (5s1p)/[3s1p] for hydrogen. This is called as basis B.

In table III.1 we report the optimized geometry and adiabatic excitation energies of the carbon mono-hydride cation (CH^+) for singlet and triplet excited state, using cc-pVDZ and cc-pVTZ basis set. We compare our results for the bond length and adiabatic excitation energy with the EOM-CCSD values. In cc-pVDZ basis we also report the full configuration interaction (FCI) values. For the singlet state we also report the experimental bond length and excitation energy. In cc-pVDZ basis set FSMRCCSD gives a bond length of 1.231 Å for the singlet state which is slightly underestimated compared to the EOM-CCSD results of 1.263 Å. As we go from cc-pVDZ to cc-pVTZ basis, bond length is reduced to 1.202 Å and 1.220 Å in FSMRCCSD and EOM-CCSD respectively. For the Singlet state our bond length is close to the experimental value of 1.234

Å, however, it is underestimated compared to the EOM-CCSD as well as FCI value. The adiabatic excitation energies cc-pVDZ basis set for the $^1\Pi$ state using FSMRCC (3.07 eV), EOM-CCSD (3.08eV), FCI (3.06 eV) are in good agreement with each other. The experimental adiabatic excitation energy (2.99 eV) for triplet state, FSMRCCSD gives a bond length of 1.146 Å, whereas EOM-CCSD gives 1.151 Å in cc-pVDZ basis. However, in case of triplet Π state, as we go from cc-pVDZ to cc-pVTZ basis, bond length is increased to 1.151 Å in FSMRCCSD. Whereas, in EOM-CCSD bond length is reduced to 1.125 Å. Triplet state excitation energy is 1.08 eV using FSMRCCSD, where as, EOM-CCSD gives 1.14 eV. As we go from cc-pVDZ to cc-pVTZ basis, adiabatic excitation energy values for the $^1\Pi$ state are decreased marginally in FSMRCCSD as well as EOM-CCSD methods. However, for the triplet state as we go from cc-pVDZ to cc-pVTZ adiabatic excitation energies are increased in both the methods.

Table III.2 reports singlet and triplet Π state results in basis B. We compare out results with EOM-CCSD and Full CI results. It can be seen that our values are in good agreement for the triplet Π state with EOM-CCSD and Full CI. Also the adiabatic excitation energies match with EOM-CCSD value. Though compared to Full CI (1.10 eV) FSMRCCSD (1.13eV) and EOM-CCSD(1.13 eV) are slightly overestimated. For the singlet state bond length and adiabatic excitation energy are marginally large compared to EOM-CCSD value. FCI over estimates the bond length compared to FSMRCCSD as well as EOM-CCSD.

Table III.1. Optimized C-H bond lengths and adiabatic excitation energies for the singlet and triplet Π state of CH^+:

State	Basis	Method	C-H bond (Å)	AEE (eV)
$^1\Pi$	cc-pVDZ	FSMRCCSD	1.231	3.07
		EOM-CCSD	1.263	3.08
		FCI	1.273	3.06
	cc-pVTZ	FSMRCCSD	1.202	3.03
		EOM-CCSD	1.220	3.07
		Experimental	1.234	2.99
$^3\Pi$	cc-pVDZ	FSMRCCSD	1.146	1.08
		EOM-CCSD	1.151	1.14
		FCI	1.160	1.05
	cc-pVTZ	FSMRCCSD	1.151	1.12
		EOM-CCSD	1.125	1.16

Table III.2. Optimized C-H bond lengths and adiabatic excitation energies for the singlet and triplet Π state of CH$^+$ using basis B^a:

State	Method	C-H bond (Å)	AEE (eV)
$^1\Pi$	FSMRCCSD	1.223	3.19
	EOMCCSD	1.238	3.15
	FCI	1.254	3.10
$^3\Pi$	FSMRCCSD	1.132	1.13
	EOMCCSD	1.132	1.13
	FCI	1.135	1.10

a: C: (10s6p1d)/[5s3p1d]. H: (5s1p)/[3s1p]

III.3.B. Water:

The ground-state RHF wave function for water is $\Psi_{ground} = 1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$. The low-lying excited states of water considered here are generated by excitations from $1b_1 \rightarrow 3Sa_1$. Model space consists of one active hole and one active particle. The singlet and triplet B_1 excited state geometries as well as adiabatic excitation energies are reported in Table III.3. Geometries are optimized in aug-cc-pVDZ basis [84]. It can be seen from the Table III.3 that FSMRCCSD predicts bond length 0.01 Å shorter compared to EOM-CCSD, CC-LRT and MRCISD method. RI-CC2 underestimates the bond length and bond angle compared to all the theoretical methods. The bond angle using FSMRCC is in good agreement with the MRCISD. EOM-CCSD and CC-LRT predict bond length slightly higher compared to FSMRCCSD and

MRCISD. The adiabatic excitation energy using FSMRCCSD (7.05 eV) is in good agreement with EOM-CCSD (7.11 eV), CC-LRT (7.10 eV), MRCISD (6.69 eV) usderestimates the adiabatic excitation energy compared to other theoretical methods.

For the $^3B_1$ state of FSMRCCSD is in good agreement with EOM-CCSD for the bond length as well as bond angle. However, CC-LRT overestimates the bond angle. The adiabatic excitation energy using EOM-CCSD and CC-LRT are in good agreement, whereas FSMRCCSD marginally over estimates.

Table III.3. Optimized geometry and adiabatic excitation energies for the singlet and triplet B_1 state of water:

State	Method	O-H bond length (Å)	H-O-H bond angle (^{0})	AEE (eV)
$^1B_1$	FSMRCCSD	1.062	103.0	7.05
	EOM-CCSD	1.072	104.5	7.11
	MRCISD	1.070	103.05	6.69
	CC-LRT	1.072	104.63	7.10
	RI-CC2	1.043	102.60	----
$^3B_1$	FSMRCCSD	1.090	107.00	6.90
	EOM-CCSD	1.097	107.10	6.59
	CC-LRT	1.10	109.66	6.62

III.3.C. Ozone:

Because of the importance of ozone is the shielding of harmful UV light, excited state ozone spectra has been studied extensively. Ozone is a challenging system, due to the strong multi-reference character of the excited states. Thus ozone serves as an ideal candidate for the test of the valance-universal MRCC theory. Geometries of the low lying singlet and triplet B_2 states of ozone are studied. We have used two basis sets for the study of $^1B_2$ state. The first basis is called basis A, consists of Dunning (10s5p)/[4s2p] contraction [85]. In addition, one d polarization function with exponent 1.211 is added. The second basis set used is aug-cc-pVDZ [84]. The RHF wave function for the ground state of O_3 molecule at the geometry of the B_2 state is given by:

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

We have chosen $1a_2$ as active hole and $2b_1$ as active particle. The model space consists of singly excited determinant within this active subspace with respect to the vacuum. The B_2 state can be characterized as a single excitation from $1a_2 \rightarrow 2b_1$. Table III.4 reports optimized geometries as well as adiabatic excitation energies of the singlet and triplet B_2 state. We compare our results in basis A with the polarization configuration interaction (POL-CI) [86] calculations in DZP basis. We also report in parenthesis adiabatic excitation energies obtained using FSMRCCSD method from our previous calculations [87] done in DZP basis. In our previous study we have reported adiabatic as well as vertical excitation energies of six low lying excited states. Adiabatic excitation energies were calculated using MCSCF-CI optimized geometries for all states including the ground state ${}^1\mathrm{A}_1$. However, in the present study of the ${}^1B_2$ state we have chosen the POL-CI optimized geometry. It can be seen from Table III.4, that POL-CI predicts slightly longer bond length and shorter bond angle compared to FSMRCCSD for the triplet B_2 state. EOM-CCSD and FSMRCCSD agree well for the bond length and bond angle for the ${}^3B_2$ state. Adiabatic excitation energies using FSMRCCSD, POL-CI and EOM-CCSD are in good agreement with each other. For the singlet state, FSMRCCSD predicts bond length of 1.391 Å which is in good agreement with the EOM-CCSD value of 1.391 Å, where as, POL-CI predicts slightly longer bond length of 1.405 Å. The bond angle of FSMRCCSD (108.5^0) is in agreement with the POL-CI (108.4^0) value. Where as, EOM-CCSD (110.9^0) overestimates it. Though the geometries of FSMRCCSD and EOM-CCSD are slightly different, the excitation energies is in good agreement with each other. POL-CI gives adiabatic excitation energy value of 5.54 eV. Our previous calculations predict adiabatic excitation energies of 4.62 eV. The difference between the old and new values is due to different ground state geometry. The ${}^1B_2$ state was also studied using aug-cc-pVDZ basis set. We compare our results with EOM-CCSD and CC-LRT. The bond length using FSMRCCSD (1.375 Å) is in good agreement with the EOM-CCSD (1.381 Å) as well as CC-LRT (1.381 Å) values. However, FSMRCCSD underestimates bond angle by $2^{\mathbf{0}}$. The adiabatic excitation energy using FSMRCSSD (4.88 eV) is in good agreement with EOM-CCSD (4.90 eV) and CC-LRT (4.96 eV).

Table III.4. Optimized geometries and adiabatic excitation energies for the singlet and triplet B_2 states of ozone:

State	**Method**	**Basis set**	**Distance (Å)**	**<O-O-O (^{0})**	**AEE (eV)**
$^3B_2(1a_2\rightarrow 2b_1)$	FSMRCCSD	DZP	1.341	108.3	0.92 (0.92)
	POL-CI[a]		1.382	107.9	0.92
	EOM-CCSD		1.345	108.7	0.95
$^1B_2(1a_2\rightarrow 2b_1)$	FSMRCCSD		1.391	108.5	4.92 (4.62)[b]
	POL-CI[a]		1.405	108.4	5.54
	EOM-CCSD		1.398	110.9	5.00
	FSMRCC	Aug-cc-pVDZ	1.375	107.0	4.88
	EOM-CCSD		1.381	109.37	4.90
	CC-LRT		1.381	109.37	4.96

a: see ref. 86.

b: see ref. 87.

α_d=1.211

III.3.D. Formaldehyde:

We report the excited state geometry of the singlet and triplet A_2 state in cc-pVDZ basis. We compare our results with EOM-CCSD, MRCISD, MRAQCC [83] and experimental [88, 89] values. Our model space consists of one active hole and one active particle. Table III.5 reports optimized geometries along with the adiabatic excitation energies. It can be seen that FSMRCCSD, EOM-CCSD and MRAQCC are in good agreement with each other for the C-O as well as C-H bond length. Theoretical and experimental C-H bond distances also agree well with each other. FSMRCCSD predicts H-C-H angle of 122.9^0. Whereas, EOM-CCSD, MRCISD and MRAQCC predicts bond angle as 123.2^0, 125.1^0 and 123.8^0 respectively, compared to the experimental value of 118.6^0. Thus, compared to experiment all the theories predict slightly higher bond angle. FSMRCCSD, MRCISD and MRAQCC agree with wach other for adiabatic excitation energy (AEE). EOM-CCSD overestimates AEE. There are no experimental results available for the triplet state so we compare our results with EOM-CCSD values. For the triplet A_2 state FSMRCCSD and EOM-CCSD agree well with each other for bond length and bond angle. Here too, EOM-CCSD predicts excitation energies slightly higher compared to FSMRCCSD.

Table III.5. Optimized bond distances (Å), bond angle (^{0}) and adiabatic excitation energies (eV) for the singlet and triplet A_2 states of formaldehyde:

State	Parameter	FSMRCCSD	EOM-CCSD	MRCISD	MRAQCC[a]	Expt.[b]
$^1A_2$	R_{CO} (Å)	1.317	1.323	1.358	1.349	1.321
	R_{CH} (Å)	1.098	1.099	1.091	1.099	1.103
	HCH (^{0})	122.9	123.2	125.1	123.8	118.6
	AEE (eV)	3.62	3.71	3.63	3.60	3.50
$^3A_2$	R_{CO} (Å)	1.304	1.316	----	----	----
	R_{CH} (Å)	1.093	1.095	----	----	----
	HCH (^{0})	124.1	124.3	----	----	----
	AEE (eV)	3.15	3.26	----	----	----

a: see ref. 83

b: see ref. 88, 89.

III.4. Conclusion:

Fock space multi reference coupled cluster method is used for geometry optimization of low-lying excited states. We also report adiabatic excitation energies to compare the optimized geometry. We compare our results for geometry with CC-LRT, EOM-CCSD, MRCISD, MRAQCC results obtained using analytic method. Our results for triplet are in good agreement with other theoretical results. For the singlet state bond angle difers by maximum of 2^0

and bond lengths are within 0.01 Å for most cases. Thus, the numerically optimized excited state geometries are in good agreement with other analytic results.

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Chapter IV

Analytic gradient formulation for doublet radical using Fock space multi-reference coupled cluster method

Abstract

The response approach using Fock space multi-reference coupled cluster method for the calculation of electric properties has been established. Electric properties of doublet radicals were obtained using Lagrange based constrained variational approach (CVA). In this chapter, we will present the CVA approach for the analytic gradients of doublet radicals. For electric properties orbital response is not crucial. However, for gradient study it is important to include orbital response. The CVA response approach will be extended for analytic gradients of doublet radicals.

IV.1. Introduction

Single reference coupled cluster (SRCC) method [1-4] has been very successful for the calculation ground state energies, properties [5-8], gradients [9-13] and potential energy surfaces [14] of closed shell molecules. Due to exponential form of the wave function, it introduces electron correlation very accurately and gives size extensive values of properties. However, for the situations where several configurations contribute equally for the accurate description of the exact wave function, *i.e*., bond-breaking situations or excited states, SRCC fails. The restricted open shell-based CC (ROHF-CC) [15] methods, which include linear approximation of triples operator, have been successful in describing the quasi-degenerate cases. Within single reference framework, in addition to full singles and doubles amplitudes selected triple and quadruple level excitations have been considered to handle quasi-degenerate [16] cases. However, multi reference (MR) or multi determinantal approach is a more general solution. MRCC [17-28] methods can be broadly classified into Fock-space or valence-universal (VU) [23-27] theories and Hilbert-space (HS) or state-universal (SU) [23] and state specific [17-22] methods. Among the multi-reference methods, effective Hamiltonian based [29, 30] methods provides multiple roots via diagonalization of the effective Hamiltonian. The Fock space MRCC method is suitable for the calculation of properties of systems with variable number of electrons *i.e* ionization potential [31], electron affinity [32], excitation energy [27, 33] in a single calculation. The Hilbert space methods are suitable for the calculation of properties of systems with fixed number of electrons and are suitable for the potential energy surface calculations [34]. However, both the methods suffer from the problem of convergence due to presence of intruder states. The intruder state problem can be handled using intermediate Hamiltonian [35] method. Intruder state problem can also be solved by using state specific multireference method developed by Mukherjee and co-workers [36].

The equation of motion coupled cluster (EOM-CC) [37-41] method extends single-reference coupled-cluster (CC) theory to calculate excited, ionized and electron-attached energies [42-49]. Coupled-cluster linear response theory (CC-LRT) [50, 51] is an alternative derivation of EOM-CC theory and both the methods are equivalent for excitation energies. Similarly, the coupled-cluster based Green's function [52] method is equivalent to EOM-CC. The symmetry-adapted cluster configuration interaction (SAC-CI) approach by Hirao and Nakatsuji [53, 54] is also closely related to EOM-CC and CC-LRT. The similarity transformed EOM-CC method (STEOM-CC), which is size extensive, was developed by Nooijen and co-workers [45, 55]. For the one valence problem, EOMCC and FSMRCC are equivalent. However, the equivalence breaks down for higher valence sectors. The spin-flip EOMCC (SF-EOM-CC) [56] method has also been introduced as a clever way to describe the multi-reference states. The method of moments coupled cluster (MMCC) [57] has also been successful in describing some quasi-degenerate problems.

To increase the scope and applicability of a method for general electronic structure calculations, it is important to have analytic response formulation which can be used for the calculation of various properties. Energy derivatives are routinely used for the potential energy surface study [14], calculation of force constant [58], for identification of maxima, minima or transition state [59]. The analytic derivates are also used for the calculation of infra red (IR) spectra [60, 61] and Raman spectra [61-64]. The Geometry optimization [65] is one of the most common task in computational chemistry and accurate geometries are of fundamental importance for accurate calculation of molecular properties. For most of the *ab inito* methods like, Hatree Fock (HF) [58a, 66, 67], multi configuration self consistent field (MCSCF) methods [67-71], density functional theory (DFT) [72], time-dependent density functional theory (TD-DFT) [73], configuration interaction (CI) [74, 75] as well as multi-reference CI (MRCI) [76, 77], symmetry-adapted cluster CI (SAC-CI) [78], perturbative methods [79], propagator method [80] and resolution of identity CC2 [81] analytic gradients are routinely available. Since electron correlation plays an important role in the accurate calculation of potential energy surfaces and gradients the analytic calculation of these using correlated methods is particularly important. Analytic gradient calculations using coupled cluster method is well established and all the problems associated with the elimination of the derivative cluster amplitudes are dealt using Z- vector method [9] or the Lagrange based constrained variation approach (CVA) [10, 82]. Both the approaches lead to the same result for first order properties. Since coupled cluster is non variational in nature we need to solve for an extra amplitudes which are perturbation independent. Thus, analytic gradient requires twice the effort of the energy calculation in coupled cluster method. Theory of analytic gradients in equation of motion coupled cluster (EOM-CC) was proposed by Stanton [83] and Szalay [84]. EOM-CC gradient was implemented by Stanton and Gauss [85]. Nooijen and co-workers [86] implemented gradients for the Similarity transformed equation of motion coupled cluster (STEOM-CC) using Lagrange approach. Using similar approach and truncating at singles doubles excitation of cluster amplitude Krylov [87] implemented gradient within spin-flip EOM-CC (SF-EOM-CC) frame work. Gwaltney [88] implemented partitioned EOM-CC. Hoffmann and co-workers [89] used a Lagrangian based approach to obtain analytic formulas for generalized Van Vleck perturbation theory (GVVPT2) energy gradients. Though analytic formulation of energy derivatives within single reference coupled cluster was developed long ago [5]. The formulation of analytic derivative methods within multi-reference framework has been a recent phenomena due to various complexities. Within MRCC framework Szalay [84] developed gradient method for Hilbert space (HS) and Fock Space (FS) MRCC frame work. Within MRCC frame work, Pittner [90] has successfully implemented gradient within multi-reference Brillouin-Weigner coupled cluster framework (MRBWCC) and Gauss and coworkers [91, 92] implemented analytic gradient withing Mk-MRCC frame work. Following the response approach of the SRCC method Pal [93] developed analytic response approach within FSMRCC framework. Applications were carried out for the one valence as well as excited state dipole moments. However, since this approach includes amplitude derivatives it was not a satisfactory. Ajitha *et al.* [94] developed Z-vector method for the $(0,1)$ sector of the Fock space for the calculation of the dipole moment. It was shown that we can only eliminate the highest sector cluster amplitude derivatives in the derivative effective Hamiltonian. The lower sector derivative cluster amplitudes will be explicitly present in the equation. It was shown that the dependence of the derivative cluster amplitudes is the one valence sector can be eliminated in the derivative effective Hamiltonian in favour of a new set of perturbation independent amplitudes only under the diagonal approximation of the effective Hamiltonian. Since elimination of the derivative cluster amplitudes could be effected only in some special cases their approach was not satisfactory. Pal and co-workers [94] also developed the algebraic elimination method to generalize the Z-vector method for SUMRCC theory. However, the Z-vector is state-dependent due to multi-state nature of MRCC theories. Thus, we loss the advantage of multi reference method of FSMRCC. Similar to the SRCC constrained variation approach (CVA) [82], Szalay [84] developed a response approach within FSMRCC framework using CVA for a complete model space for analytic gradient calculation. Shamasundar *et al.* [95, 96] formulated Lagrange based response approach for valence universal [95] as well as state universal [96] multi-reference coupled cluster methods. This approach was applicable to complete and incomplete model space. CVA-FSMRCC approach was extensively tested for the first and second derivative of energy of the doublet radicals and excited states, when the perturbation was electric field [97, 98]. We will extend the CVA-FSMRCC response formulation for the calculation of analytic gradients of doublet radicals. In this chapter we will give working equations for the analytic gradients of one valence problem.

IV.2. Theory:

Fock space multi-reference coupled cluster (FSMRCC) theory is based on the concept of a common vacuum and valence universal wave operator. In the FSMRCC, N electron restricted Hartree–Fock (RHF) is chosen as a vacuum. With respect to this vacuum holes and particles are defined, which are further divided into active and inactive holes and particles. The model space, in general, is a linear combination of important determinants, with p active particles and h active holes. Such a model space belongs to the (p,h) sector of the Fock space. The model space wave function can be written as:

$$\left|\Psi_{\mu}^{(0)(p,h)}\right\rangle = \sum_{i} C_{\mu i}^{(p,h)} \left|\Phi_{i}^{(p,h)}\right\rangle \tag{IV.1}$$

where C's are the model space coefficients for the model space $\Phi_i^{(p,h)}$. With p active particles and h active holes. The dynamic correlation is introduced through the wave operator which takes the model space to the exact wave function:

$$\left|\Psi_{\mu}^{(p,h)}\right\rangle = \Omega \left|\Psi_{\mu}^{(0)(p,h)}\right\rangle \tag{IV.2}$$

The wave operator Ω can be written as:

$$\Omega = \left\{\exp\left(\tilde{T}^{(p,h)}\right)\right\} \tag{IV.3}$$

Where, curly bracket denotes the normal ordering of the operators in it. The Ω should contain cluster operators $\tilde{T}^{(p,h)}$ which are defined as:

$$\tilde{T}^{(p,h)} = \sum_{k=1}^{p} \sum_{l=0}^{h} T^{(k,l)} \tag{IV.4}$$

The cluster operator $T^{(k,l)}$ is capable of destroying exactly k active particles and l active holes, in addition to creation of holes and particles. Thus, the $\tilde{T}^{(p,h)}$ contains all the lower $T^{(k,l)}$ operators. To define effective Hamiltonian, the Bloch equation [99] is adopted, which is also used to solve the cluster amplitudes. For (p,h) sector the Bloch equation can be defined as:

$$P^{(k,l)}\left[H\Omega - \Omega H_{eff}^{(k,l)}\right]P^{(k,l)} = 0$$

$$Q^{(k,l)}\left[H\Omega - \Omega H_{eff}^{(k,l)}\right]P^{(k,l)} = 0 \tag{IV.5}$$

$$\forall k = 0,\ 1; \quad l = 0,\ 1$$

The Fock space Bloch equation is solved using subsystem embedding condition (SEC) [100]. The projection of the Bloch equation to the model space defines effective Hamiltonian where as projection to the Q space gives equation for the cluster amplitudes. Use of Bloch equation avoids the requirement of the Ω^{-1} which may not exists in some cases. The effective Hamiltonian $\left(H_{eff}\right)$ is non hermitian, the diagonalization of the effective Hamiltonian $\left(H_{eff}\right)$ within P space gives the energies of the multiples states of our interest.

$$\tilde{C}^{(k,l)}C^{(k,l)} = C^{(k,l)}\tilde{C}^{(k,l)} = 1 \tag{IV.6}$$

We have truncated the FSMRCC amplitudes at singles doubles level (FSMRCCSD).

IV.3. FSMRCCSD analytic gradient:

In FSMRCCSD method the exact energies are obtained via diagonalization of the effective Hamiltonian. The eigen value of equation for the effective Hamiltonian for one active hole and zero active particle (electron detached state) can be written as:

$$\begin{aligned}(H_{eff}^{(0,1)})_{ij} &= \left\langle \Phi_i^{(0,1)} \middle| H\Omega \middle| \Phi_j^{(0,1)} \right\rangle \\ &= P^{(0,1)} H\Omega P^{(0,1)}\end{aligned} \qquad \text{(IV.7)}$$

Since effective Hamiltonian in general we have left and right eigen vectors.

$$\begin{aligned}&H_{eff}^{(0,1)} C^{(0,1)} = EC^{(0,1)} \\ &=> E = \tilde{C} H_{eff} C\end{aligned} \qquad \text{(IV.8)}$$

$$\tilde{C} H_{eff}^{(0,1)} = E\tilde{C}^{(0,1)} \qquad \text{(IV.9)}$$

Subject to the condition Equation (IV.6)

Differentiating Equation (IV.8) gives:

$$E^{(1)} = \tilde{C}^{(1)} H_{eff}^{(0,1)} C + C^{(0,1)} H_{eff}^{(0,1)\,(1)} C^{(0,1)} + \tilde{C}^{(0,1)} H_{eff}^{(0,1)} C^{(0,1)(1)} \qquad \text{(IV.10)}$$

Where, C’s are model space coefficients. The derivative of effective Hamiltonian involves derivative Hamiltonian and wave function derivative. Since energy derivative involves model space coefficient derivative, we have to calculate energy derivative for a specific μ-th state. So, here the advantage of calculation of multiple state at a time is lost. Thus, we can write:

$$\frac{dE}{dg} = \frac{dH_{eff}^{(0,1)}}{dg} + \frac{\partial E}{\partial C}\frac{\partial C}{\partial g} \qquad \text{(IV.11)}$$

Where, g is perturbation. The first term is explicit derivatives of the effective Hamiltonian with respect to perturbation. The second term is the derivative of the model space coefficients. The derivative of the effective Hamiltonian with respect to perturbation can be expressed as:

$$\begin{aligned}\frac{dH_{eff}^{(0,1)}}{dg} = \frac{\partial H_{eff}^{(0,1)}}{\partial g} + \frac{\partial H_{eff}^{(0,1)}}{\partial T^{(0,0)}}\frac{\partial T^{(0,0)}}{\partial g} + \\ \frac{\partial H_{eff}^{(0,1)}}{\partial T^{(0,1)}}\frac{\partial T^{(0,1)}}{\partial g} + \frac{\partial H_{eff}^{(0,1)}}{\partial c}\frac{\partial c}{\partial g}\end{aligned} \qquad \text{(IV.12)}$$

Where,

$$\frac{\partial H_{eff}^{(0,1)}}{\partial g} = \sum_{pq} h_{pq}(g)\gamma_{pq} + \frac{1}{4}\sum_{\substack{pq\\rs}} \langle pq \| rs \rangle (g)\Gamma_{pqrs} \qquad \text{(IV.13)}$$

One particle density:

$$\gamma_{pq} = \langle \Phi_0 | \left(1 + \Lambda^{(0,0)} + \Lambda^{(0,1)}\right) e^{-\left(T^{(0,0)}+T^{(0,1)}\right)} p^\dagger q e^{T^{(0,0)}+T^{(0,1)}} | \Phi_0 \rangle \qquad \text{(IV.14)}$$

Two particle density:

$$\Gamma_{pqrs} = \langle \Phi_0 | \left(1 + \Lambda^{(0,0)} + \Lambda^{(0,1)}\right) e^{-\left(T^{(0,0)}+T^{(0,1)}\right)} p^\dagger q^\dagger s r e^{T^{(0,0)}+T^{(0,1)}} | \Phi_0 \rangle \qquad \text{(IV.15)}$$

Where, $\Lambda's$ are deexcitation operators. For singles doubles approximation Λ can be written as:

$\Lambda = \Lambda_1 + \Lambda_2$. Λ_1 and Λ_2 are expressed as:

$$\Lambda_1^{(0,0)} = \sum_{ia} \Lambda_a^i \left\{ i^\dagger a \right\} \qquad \text{(IV.16)}$$

$$\Lambda_2^{(0,0)} = \frac{1}{4}\sum_{\substack{ij\\ab}} \Lambda_{ab}^{ij} \left\{ i^\dagger j^\dagger b a \right\} \qquad \text{(IV.17)}$$

The first term of Equation (IV.12) is Hellmann-Feynmann term, which has explicit perturbation dependence. The second and third terms are the amplitude response terms and the last term is the orbital response term. These terms can be eliminated using Z-vector method or using the Lagrange formulation. We will be using the Lagrange formulation. The Lagrangian for the one valence problem with one active hole and zero active particles can be written as:

$$\begin{aligned}
&\Im_{\mu} = \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} \left(H_{eff}^{(0,1)} \right)_{ij} C_{j\mu}^{(0,1)} + \\
&P^{(0,1)} \Lambda^{(0,1)} Q^{(0,1)} Q^{(0,1)} \left[H\Omega - \Omega H_{eff} \right] P^{(0,1)} + \\
&P^{(0,0)} \Lambda^{(0,0)} Q^{(0,0)} Q^{(0,0)} H\Omega P^{(0,0)} - \qquad \text{(IV.18)} \\
&E_{\mu} \left(\sum_{ij} \tilde{C}_{\mu i}^{(0,1)} C_{j\mu}^{(0,1)} - 1 \right) + \\
&\sum_{pq} \lambda_{pq} \left(F_{pq} - \delta_{pq} \right) + \sum_{pq} \zeta_{pq} \left(S_{pq} - \delta_{pq} \right)
\end{aligned}$$

Here F and S are Fock and Overlap matrix respectively in MO basis. Λ, λ and ζ are Lagrange undetermined multipliers.

$$F_{pq} = \langle p | h | q \rangle + \sum_{j} \langle pj || qj \rangle \qquad \text{(IV.19)}$$

$$S_{pq} = \left\langle \Phi_p \middle| \Phi_q \right\rangle \qquad \text{(IV.20)}$$

The Lagrangian is made stationary with respect to Λ, λ and ζ *i.e,*

$$\begin{aligned}
&\frac{\partial L}{\partial \Lambda} = 0 \\
&\frac{\partial L}{\partial \lambda} = 0 = F_{pq} - \delta_{pq} \qquad \text{(IV.21)} \\
&\frac{\partial L}{\partial \zeta} = 0 = S_{pq} - \delta_{pq}
\end{aligned}$$

All the parameters of the Lagrangian are perturbation dependent. The first term gives the amplitude equation. Differentiation with respect to T $\{T^{(0,0)},\ T^{(0,1)}\}$ gives equations for the Λ. The second and third equation are equivalent to the Hartree Fock equations. If we include all the orbitals as active orbitals then the energy is invariant with respect to the unitary transformation among the occupied orbitals *i.e.* $\Lambda_{ij} = 0$. Similarly for $(1,0)$ sector of the Fock space if we choose all the particles as the active orbitals then $\Lambda_{ab} = 0$. However, in general that is not true for the Fock space calculations. Using the stationarity of Lagrangian with respect to all the parameters in it the equation, the derivative of Lagrange can be written as:

$$\begin{gathered}
\mathfrak{I}^{(1)} = \left(\tilde{C}^{(0,1)(0)} H_{eff}^{(0,1)(1)} C^{(0,1)(0)}\right)_{\mu\mu} + \\
P^{(0,1)}\Lambda^{(0,1)(0)}\left[H^{(1)}\Omega^{(0)} - \Omega^{(0)}H_{eff}^{(0,1)(1)}\right]P^{(0,1)} + \\
P^{(0,0)}\Lambda^{(0,0)(0)}H^{(1)}\Omega^{(0)}P^{(0,0)} + \\
\sum_{pq}\lambda_{pq}^{(0)}F_{pq}^{(1)} + \sum_{pq}\zeta_{pq}^{(0)}S_{pq}^{(1)}
\end{gathered} \tag{IV.22}$$

The derivative effective Hamiltonian does not contain any term from derivatives of the cluster amplitudes. The gradients can be obtained using Ω and Λ-amplitudes only. The amplitude response equations will be obtained by making Lagrange stationary with respect to cluster amplitudes. The orbital response multipliers λ and ζ will be determined by making Lagrange stationary with respect to atomic to molecular orbital coefficients, c's, *i.e.* $\frac{\partial L}{\partial c}$.

Following the strategy similar to the Levchenko *et al*. [87] we obtain the equations for the orbital response multipliers Ω and Λ as following:

Equation for λ_{ia}:

$$\begin{aligned}
&\lambda_{ia}\left(\varepsilon_a-\varepsilon_i\right)+\left\langle ik\middle|aj\right\rangle\lambda_{jk}+\left\langle ib\middle|ac\right\rangle\lambda_{bc}+\\
&\sum_{jb}\lambda_{jb}\left(2\left\langle ib\middle|aj\right\rangle-\left\langle ib\middle|ja\right\rangle\right)+\sum_{jb}\lambda^{*}_{jb}\left(2\left\langle ij\middle|ab\right\rangle-\left\langle ij\middle|ba\right\rangle\right)+\\
&\sum_{jk}\gamma_{jk}\left(-2\left\langle ij\middle|ak\right\rangle+\left\langle ij\middle|ka\right\rangle\right)+\sum_{jb}\gamma_{jb}\left(2\left\langle ib\middle|aj\right\rangle-\left\langle ib\middle|ja\right\rangle\right)+\\
&\sum_{jk}\gamma^{*}_{jb}\left(-2\left\langle ij\middle|ab\right\rangle-\left\langle ij\middle|ba\right\rangle\right)+\sum_{bc}\gamma_{bc}\left(2\left\langle ib\middle|ac\right\rangle-\left\langle ib\middle|ca\right\rangle\right)+\\
&\sum_{jbc}\left(2\left\langle bc\middle|aj\right\rangle-\left\langle bc\middle|ja\right\rangle\right)\Gamma_{ijbc}+\sum_{jkb}\left\langle ib\middle|jk\right\rangle\left(-2\Gamma_{jkab}+\Gamma_{kjab}\right)+\\
&\sum_{jkb}\left(-2\left\langle jk\middle|ab\right\rangle-\left\langle jk\middle|ba\right\rangle\right)\Gamma^{(0,1)}_{jikb}=0
\end{aligned} \tag{IV.23}$$

Equation for λ_{ab}:

$$\begin{aligned}
&\lambda_{ab}\left(\varepsilon_a-\varepsilon_b\right)+2\gamma_{ab}\left(\varepsilon_a-\varepsilon_b\right)+\sum_{ijc}\left(-2\Gamma_{ijbc}+\Gamma_{ijab}\right)\left\langle ac\middle|ij\right\rangle\\
&+\sum_{ijc}\left(2\left\langle ij\middle|bc\right\rangle+\left\langle ij\middle|cb\right\rangle\right)\Gamma^{*}_{acij}=0
\end{aligned} \tag{IV.24}$$

This equation the constrained imposed is $a\neq b$

Equation for λ_{ij}:

$$\begin{aligned}&\lambda_{ij}\left(\varepsilon_i-\varepsilon_j\right)+2\gamma_{ij}\left(\varepsilon_i-\varepsilon_j\right)+\sum_{kab}\left(2\langle ab|ik\rangle-\langle ab|ki\rangle\right)\Gamma_{jkab}+\\&\sum_{ka}\Lambda_{ka}^{(0,0)}\left(2\langle jk|ia\rangle-\langle jk|ai\rangle\right)+\sum_{abk}\langle ab|jk\rangle\left(2\Gamma^{*}_{abik}-\Gamma^{*}_{abki}\right)+\\&\sum_{kb}\gamma_{kb}\left(2\langle jb|ik\rangle-\langle jb|ki\rangle\right)+\sum_{kla}\langle kl|ja\rangle\left(-2\Gamma_{kila}^{(0,1)}+\Gamma_{lika}^{(0,1)}\right)+\\&\sum_{kla}\Gamma^{*}_{jakl}\left(-2\langle kl|ia\rangle+\langle kl|ai\rangle\right)=0\end{aligned}\tag{IV.25}$$

This equation the constrained imposed is $i \neq j$

Equation for ω_{ia}:

$$\begin{aligned}&\omega_{ia}+\frac{1}{2}\varepsilon_i\lambda_{ia}+\varepsilon_i\gamma_{ia}+\\&\sum_{jbc}\left(2\langle bc|aj\rangle-\langle bc|ja\rangle\right)\Gamma_{ijbc}+\sum_{jkb}\langle ib|jk\rangle\left(-2\Gamma_{jkab}+\Gamma_{jkba}\right)+\\&\sum_{jkb}\Gamma_{jikb}^{(0,1)}\left(-2\langle jk|ab\rangle+\langle jk|ba\rangle\right)=0\end{aligned}\tag{IV.26}$$

Equation for ω_{ij} :

$$
\begin{aligned}
&\omega_{ij} + \varepsilon_i \delta_{ia} + \frac{1}{2}\varepsilon_i \lambda_{ij} + \varepsilon_i \gamma_{ij} \\
&\sum_{ka} \lambda_{ka} \left(2\langle jk|ia\rangle - \langle jk|ai\rangle \right) + \sum_{ak} \gamma_{ka} \left(2\langle jk|ia\rangle - \langle jk|ai\rangle \right) + \\
&\sum_{kab} \left(2\langle ab|ik\rangle - \langle ab|ki\rangle \right) \Gamma_{jkab} + \sum_{kab} \langle ab|jk\rangle \left(2\Gamma^{*}_{abik} - \Gamma_{abkl} \right) + \\
&\sum_{kla} \langle kl|ja\rangle \left(-2\Gamma^{(0,1)}_{kila} + \Gamma_{lika} \right) + \sum_{kla} \Gamma_{jakl} \left(-2\langle kl|ia\rangle + \langle kl|ai\rangle \right) = 0
\end{aligned}
\tag{IV.27}
$$

Equation for ω_{ab} :

$$
\begin{aligned}
&\omega_{ab} + \varepsilon \gamma_{ab} + \frac{1}{2}\varepsilon_a \lambda_{ab} \\
&\sum_{kab} \langle ac|ij\rangle \left(-2\Gamma_{ijbc} + \Gamma_{ijcb} \right) + \sum_{ijc} \Gamma^{*}_{acij} \left(-2\langle ij|bc\rangle + \langle ij|cb\rangle \right) \\
&\sum_{icd} \langle ia|dc\rangle \left(2\Gamma^{*}_{cdbi} - \Gamma^{*}_{cdib} \right) = 0
\end{aligned}
\tag{IV.28}
$$

The CVA method is a single-root method. The Λ amplitudes depend on the desired state of the molecule. Therefore, for every state one has to calculate the Λ amplitudes separately. 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 . The Fock space equations are decoupled for each sector. The T amplitude equations are decoupled from the Λ equations, however, Λ equations are coupled with the T amplitudes. It may be noticed that the coupling within the Λ amplitudes in various valence sectors is exactly opposite of SEC. Thus, one has to solve for the Λ amplitudes successively from the highest valence sector to the lowest valence sector. Evaluation of gradients involve derivative of one and two electron integrals. These quantities depend upon the first order response of Hamiltonian in the atomic orbital basis and the molecular orbital coefficients. The later is avoided through Z vector approach or Lagrange approach. The effective one and two particle densities are constructed and back transformed to atomic basis to contract with the derivative and one and two electron integrals. The general procedure to be followed is:

1) Solve Hartree Fock equations.

2) Transform one and two electron integrals in MO basis

3) Evaluate CCSD equations and construct the $\bar{H}$

4) Solve Lambda equations (IV.18)

5) Evaluate one and two particle densities

6) Solve Z-vector equation for eliminating orbital response and construct the relax density matrices.

7) Add the relax density matrices with SCF and CC density matrices to construct total density matrices.

8) Back transform the total one and two particle densities to atomic basis.

9) calculate derivative overlap, one and two electron integrals in the atomic basis. Contract them with the densities to get the analytic derivatives of the energy *i.e*. gradients.

Similar equations can be derived for doublet radicals with electron attached states.

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CHAPTER V

Scope and goal of the thesis

Abstract:

This chapter deals with future prospects of the work presented in the thesis. The thesis mainly involves the application of Fock space multi-reference method for the calculation of life-time of resonance states and geometry optimization of excited states and doublet radicals. FSMRCC method is known to give accurate spectroscopic energies. This method includes dynamic and non-dynamic electron correlation in a consistent manner to give accurate difference energies. Thus, FSMRCC is best suited for the calculation of properties of doublet radicals and excited states.

V.1. Future prospects:

Chapter I gives a comprehensive review of electronic structure methods for atoms and molecules. We started our discussion with the Born-Oppenheimer approximation (BOA) [1], which simplifies the electronic structure calculation by freezing the motion of nuclei. We have focused our discussion on the Hartree-Fock (HF) or SCF method [2-5]. The HF method simplifies the electronic structure calculation by assuming the N-electron wave function as a single Slater determinant. HF method recovers 95% of the total energy, however, it fails in some cases to give even qualitative trend correct. These are cases where the correlation energy plays an important role, even though it is a small fraction of the total energy. Thus, we need to go beyond HF method for more accurate calculation of N-electron system. Electron correlation of anti-parallel spins is not included in the HF method. We have discussed correlated methods like, configuration interaction (CI) [6], many body perturbation theory (MBPT) [7-11] and coupled cluster theory (CC) [12-15]. In the introduction we have emphasized on the state-of-the-art CC method and discussed the advantages of CC methods over other methods to calculate correlation energy. The single reference methods include the static correlation exactly, but for excited states and closed shell molecules away from equilibrium, where no single determinant is dominant, the single reference methods fail. In such cases multi reference description becomes necessary. In section I.9 we have discussed the multi reference based [16-29] coupled cluster methods.

The thesis involves calculation of various properties using Fock space multi reference coupled cluster method. The properties in which we are interested are:

1. The position and life time of resonances.

2. Geometry optimization of low lying excited states dominated by hole-particle excitation using numerical differentiation.

3. Analytic formulation and implementation for geometry optimization of doublet radicals.

Resonance states are temporary bound states. Since these are decaying states, they do not belong to the Hermitian domain of the Hamiltonian. Thus, normal bound state methods cannot be used to study resonance states. With the help of analytic continuation of the Hamiltonian the problem is transformed, so that the bound state methods can be used. The analytic continuation was done by using complex absorbing potential (CAP) [30, 31] in FSMRCC method, truncated at singles and doubles level (FSMRCCSD). This method is known as CAP-CIP-FSMRCCSD [32]. The study was done at the equilibrium geometry of the target molecule. We can study the life time of the shape resonance as a function of geometry. Study of complex potential energy surface is also useful for the study of orientation of the adsorbate molecule on crystal structure.

Analytic gradients are useful in geometry optimization. We have presented equations for the analytic gradients of doublet radicals. The formulation can be used for cation or anion. The approach is based on Lagrange based method and is a very general one. This can easily be extended for higher order derivatives. The method can also be extended for the excited states geometry optimization. We have successfully implemented this approach for first and second derivatives, when external perturbation is electric field. This same approach can be used for the calculation of mixed derivatives. Table V.1 lists the derivatives and the corresponding properties that can be calculated using analytic gradients.

Table V.1. List of properties can be calculated using gradient:

Derivative	Properties can be calculated
$\frac{dE}{dx_i}$	Forces on nuclei, stationary points on potential energy surface. Equilibrium and transition state structure.
$\frac{d^2E}{dx_i dx_j}$	Harmonic force constants, harmonic-vibrational frequencies.
$\frac{d^3E}{dx_i dx_j dx_k}$	Cubic force constants, vibrational corrections to distances and rotational constants.
$\frac{d^4E}{dx_i dx_j dx_k dx_l}$	Quartic force constants, anharmonic corrections to vibrational frequencies.
$\frac{d^2E}{dx_i d\varepsilon_\alpha}$	Dipole derivative, infra red intensities within harmonic approximation.
$\frac{d^3E}{dx_i d\varepsilon_\alpha d\varepsilon_\beta}$	Polarizability derivative, Raman intensity

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List of publications

PEER-REVIEWED JOURNALS

1. Fock space multi-reference coupled cluster theory: Study of shape resonance

Sumantra Bhattacharya, Nayana Vaval, Sourav Pal*, Int. J. Quantum Chem. (accepted)

2. Shape resonance in electron- H_2 collision: Fock space multi reference coupled cluster method

Sumantra Bhattacharya, Nayana Vaval, Sourav Pal* (manuscript under preparation)

3. Excited state geometry optimization: Fock-Space Multi Reference Coupled Cluster method

Sumantra Bhattacharya, Achintya Kumar Dutta, Nayana Vaval, Sourav Pal* (Communicated)

4. Geometry optimization of doublet radical: using analytic gradient method within Fock space multi reference coupled cluster method

Sumantra Bhattacharya, Achintya Kumar Dutta, Nayana Vaval, Sourav Pal* (Manuscript under preparation)

Book chapter

1. Static hyper-polarizability of open shell molecules computed at the FSMRCCSD level using constrained variational approach

A. Bag, **S. Bhattacharya**, S. Pal in ‘*Recent Advances in Spectroscopy Theoretical, Astrophysical and ExperimentalPerspectives’* edited by R. K. Chaudhuri, M.V. Mekkaden, A. V. Raveendran, A. Satya Narayanan, (Springer-Verlag, Berlin, 2009) p. 99.

Errata

Errata