Multi-reference coupled-cluster studies on the effect of dynamical and non-dynamical correlation on molecular energies and properties

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CERTIFICATE FROM THE SUPERVISOR(S)

This is to certify that the thesis entitled "Multi-reference coupled-cluster studies on the effect of dynamical and nondynamical correlation on molecular energies and properties" submitted by Smt. Sangita Sen who got her name registered on 12-04-2011 for the award of Ph.D. (Science) degree of Jadavpur University, is absolutely based upon her own work under the supervision of Professor Debashis Mukherjee and Dr. Ankan Paul and that neither this thesis nor any part of it has been submitted for either any degree/diploma or any other academic award anywhere before.

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Dedicated to

those who have cared

PREFACE

The non-relativistic Schrödinger Hamiltonian is spin-free and ought to generate wave-functions which are eigenfunctions of S^2. Since, molecular properties are defined in a perturbative framework, it is pertinent that the wave-function corresponding to the zeroth order spin-free Hamiltonian be properly spin-adapted even if the perturbation breaks the spin-eigenfunction nature of the wave-function eventually. Thus, the development of electronic correlation theories which in addition to maintaining the basic requirements of accuracy and size-extensivity generates a properly spin-adapted approximate wave-function is a worthy pursuit. Coupled cluster theory of both the single-reference and the multi-reference type have emerged as effective tools for estimating the electronic correlation energy in molecules wherein the multi-reference theories have the advantage of being able to handle molecular states which do not have a dominant single determinantal representation.

In this thesis we have formulated and implemented a suite of related multi-reference coupled cluster theories to describe open-shell molecular systems taking care to maintain spin-adaptation of the wave-function and incorporate the effects of electron correlation and orbital relaxation to the greatest extent possible within the limits of computational and theoretical viability. A spin-free unitary group adapted Jeziorski-Monkhorst type of Ansatz has been developed and applied in the State-Universal Multi-Reference Coupled-Cluster (SUMRCC) framework to determine energies of excited states and electron attached/detached states. We call our method as the Unitary Group Adapted State Universal Multi-reference Coupled Cluster (UGA-SUMRCC) theory, the study and ramifications of which form the basic substance of this thesis. A thorough investigation of the role of different terms in the equations, the choice of the excitation manifold and the trends to be expected from various approximations of the theory is undertaken.

In the UGA-SUMRCC theory, we have used a normal-ordered multi-exponential type wave operator Ansatz with spin-free excitations in the cluster operators. It generates a spin-adapted CC function and has a terminating expression of the so-called 'direct term' at the quartic power of cluster amplitudes. The exponentiation of relaxation inducing operators is expected to be able to describe orbital- and correlation-relaxation effectively. We investigate this aspect by applying our formalism to study ionized/excited state energies involving core electrons which subjects the molecule to a large orbital- and correlation-relaxation. The high degree of orbital relaxation attendant on removal of a core electron and the consequent correlation relaxation of the ionized state are found by us to be captured very effectively with the Hartree-Fock orbitals for the neutral ground state using our UGA-SUMRCC. The UGA-QFMRCC uses a related factorized Ansatz which allows us to drop the correlated ground state energy from the expressions thereby yielding energy differences directly.

For studying low-lying excitation energies, we have used h-p excited CSFs relative to the closed-shell HF state. The model space thus generated is a special type of incomplete model space (IMS), and we have formulated an explicitly size-extensive formulation for the excited states, following earlier theories of Mukherjee, which advocate the abandoning of the customary intermediate normalization of the wave operator. We have delineated the non-trivial modifications of our formalisms in this context.

Since the core electrons are more severely affected by relativity, we have undertaken to study the importance of scalar relativistic effects on core ionization and excitation energies in the context of a spin-free Dirac-Coulomb Hamiltonian. The effects are found to be significant even for small molecules such as water and the effect increases as we move to molecules containing medium-heavy atoms as expected.

We also present in this thesis, a formulation of the analytic gradients for the single open-shell limit of the UGA-SUMRCC which we call UGA-OSCC. As a preliminary demonstration of the accuracy in properties to be expected from this formulation we present electric dipole moments and polarizabilities of some small molecules computed using numerical gradients.

We find that the two theories developed by us in this thesis, viz. UGA-SUMRCC and UGA-QFMRCC can yield spectroscopic energy differences with chemical accuracy. It is remarkable that the theories can provide very accurate core electron ionization potentials even when the orbitals of the neutral molecule are used. The theories are quite stable giving the same degree of accuracy for the variety of molecular states studied by us in this thesis and we are optimistic of further developments on them.

IACS *Sangita Sen*
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TABLE OF CONTENTS

Chapter 1

Overview and Scope of the Thesis

1.1 The Premise

Quantum Chemistry of atoms and molecules, is today primarily a search for balance. While this is a field which bridges our understanding of physical interactions and our observation of physical and chemical phenomena, the interplay of a myriad diverse interactions at varied length and energy scales makes it imperative for us to not only understand them individually but also to adjudge their relative role in shaping the phenomenon under study. Quantum Chemistry, in general, and Electronic Structure and Dynamics in particular have maintained a steady growth rate over the last five decades pushing the frontiers of theoretical and computational research into the experimental laboratories. Theories of Electronic Structure and Dynamics are now routinely used in understanding experimental findings and have in several instances encouraged new experiments. The challenge facing theoreticians today is to encompass diversity in the time and length scale of interactions, the energy ranges for different phenomena and the idiosyncrasies of molecular states, all within the limitations of computational technology and resources. While a single theoretical framework to do it all seems unlikely in the current scenario, much has been achieved in various directions. The formulation of sophisticated methodologies has kept pace with the rapid evolution of computers and algorithms and we can now not only venture to compute spectroscopic parameters, reaction pathways and other quantities related to the energetics of molecules but also the response of atoms and molecules to external perturbations.

The Schrödinger equation is the center piece of electronic structure theories and the impossibility of solving it analytically for even a two-body Hamiltonian makes it intriguing to find out the best possible approximate solution. Although potentially exact theories exist, their viability for molecules of even moderate size is unlikely and the search for approximate theories continues unabated. Accuracy and computational cost are the two main watchwords for the viability of any current or future theory. Accuracy implies the correct modeling of the physical interactions governing a molecule and may be translated into a number of desirable characteristics of a theory such as systematically improvable accuracy, physically interpretable terms, proper balance between different types of interactions, correct scaling of the energy with system size and satisfying known limits of the energy and the wave function. We shall discuss these issues in more concrete terms once the necessary terminologies have been introduced. While the computational cost will increase with system size, the different theories have a different rate of increase called the formal “scaling” of the theory and the focus is on achieving as low a scaling as possible. Both theoretical considerations and algorithmic developments play an important role in this regard.

An electronic state is fully represented by a wave-function which satisfies the Schrödinger equation of its Hamiltonian. It thus has three inter-dependent ingredi-

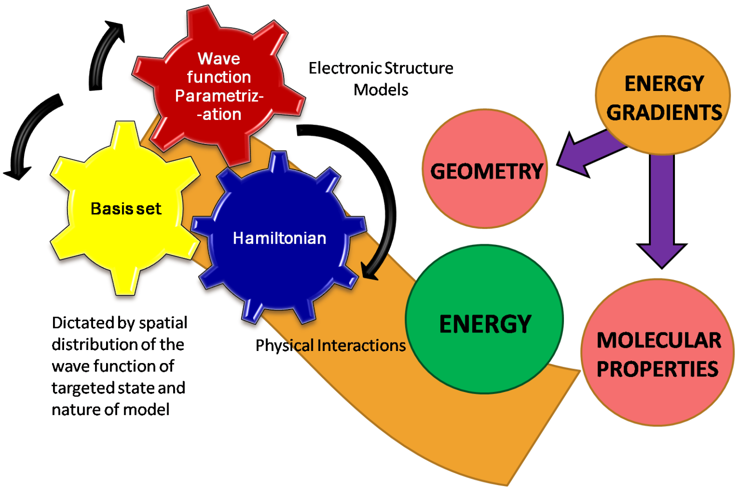

Figure 1.1: **Ingredients for electronic structure theories**

ents: a Hamiltonian representing the interactions among the particles in the molecular system, a basis set which provides a finite function space for describing the wave function (which is, in principle, infinite) and a formal parametrization of the many-body wave function with variables in some functional form conforming to physical requirements of the wave function and enabling easy determination of the variables via the Schrödinger equation. All three ingredients are available in hierarchies of accuracy and are required in different proportions for different situations. Fig. 1.1 is a pictorial depiction of the possible choices.

The Hamiltonian for a molecule involves interactions among nuclei and electrons. The mass and velocity scales of the nuclei are, in general, very different from that of the electrons. Thus, the nuclear degrees of freedom can be decoupled from the electronic degrees of freedom by what is called the Born-Oppenheimer (BO) approximation and the total molecular wave function may be written as a product of the nuclear wave function and the electronic wave function each containing the information of the other in a parametric form. The BO approximation is implicit in all electronic structure theories and the corresponding electronic Hamiltonian is called the *Adiabatic Hamiltonian* [1]. A plot of the energy of an electronic state against nuclear geometry constitutes the potential energy surface (PES) for the motion of the nuclei. However, situations often arise where the BO approximations are invalid such as at conical intersections of adiabatic states and in order to account for Jahn-Teller effects in molecules and one must shift to a self-consistent solution for the nuclear and electron wave-function by using what is called a *Diabatic Hamiltonian* [2]. In all the following discussions we restrict ourselves to only those situations where the BO approximation is valid.

Within the BO approximation, the electronic Hamiltonian has a clear hierarchy ranging from the non-relativistic (NR) Schrödinger Hamiltonian through the relativistic (Rel) Dirac Hamiltonian and finally to the full Hamiltonian inclusive of quantum electrodynamic (QED) effects [3, 4, 5, 6]. Spin being a manifestation of the relativistic behavior of electrons, the NR Schrödinger Hamiltonian is spin-free and hence, no spin-dependent interactions feature in it. Consequently, the corresponding wave function is an ordinary function of complex variables and an eiqenfunction of the S^2, spin operator. Pauli constructed a Hamiltonian using matrices to mimic the effect of spin-dependent interactions (the Pauli spin matrices) leading to what is called the *Pauli Hamiltonian* or the *Pauli-Schrödinger Hamiltonian* [7]. The wave functions obtained as a solution of the Pauli equation for a single electron have 2-components and are called spinors. Dirac in 1928 formulated the fully relativistic Hamiltonian for a free electron [8] leading to the emergence of spin as a consequence of the union of quantum mechanics and special relativity and the eventual discovery of the positron. On solution of the Dirac equation one obtains wave functions which are vectors of four complex numbers (known as bispinors), two of which resemble the Pauli wavefunction in the non-relativistic limit, in contrast to the Schrödinger equation which describes wave functions of only one complex value. Dirac's theory provided an interconnect between Pauli's phenomenological theory of spin justifying its multi-component wave-functions and the Weyl equation [9] which can be obtained as the zero mass limit of the Dirac equation. In this thesis, we will largely concentrate on the use of the Schrödinger Hamiltonian but some studies using spin-free relativistic Hamiltonians (ie. considering scalar relativistic effects) have been carried out for specialized applications where such effects were deemed important.

The basis sets, of course, are a vital component of an electronic structure theory and must be chosen not only in concurrence with the choice of the Hamiltonian and the parametrization of the wave function but also keeping in mind the information one wishes to extract from the electronic wave function. For example, a general thumb rule is that one requires more diffuse functions to describe anions and Rydberg-like excited states than one needs for the ground state (GS). Also, an accurate computation of electrical properties requires a basis set containing functions of higher angular momentum and for magnetic properties the question of guage-independence must be suitably handled. There are a large number of specialized basis sets available and although we shall be careful in our choices we will not discuss this aspect in detail unless necessary. An extensive discussion may be found in the book by Helgaker et al. [10]

The new developments presented in this thesis relate to the last ingredient - the choice of parametrization for the wave-function which is closely related to the choice of the Hamiltonian. The following quote puts the difficulty of representation of a many-electron wave function into perspective.

". . .The solution is a function of 3N variables, even if it were possible to evaluate such a solution to any degree of numerical accuracy required, no satisfactory way of presenting the results is known. . . . the full specification of a single wave function of neutral Fe is a function of seventy eight variables. It would be rather crude to restrict to ten the number of values of each variable at which to tabulate this function, but even so, full tabulation of it would require 10^{78} *entries, and even if this number could be reduced somewhat from considerations of symmetry, there would still not be enough atoms in the whole solar system to provide the material for printing such a table."*
\- Hartree (1948)

The path that has been adopted with great success is to first take recourse to the simplest possible model - the Independent Particle Model (IPM) in this case - and then carry out systematic corrections to it. A hierarchy of theories, which constitute what is called the *ab initio* group of methods, is built on the premise that a mean-field description of an electron in the field of the nuclei and the other electrons in a molecule is the most convenient starting point for theoretical realization of the electronic state and the short-range electron-electron interactions may be modeled at varying degrees of accuracy on top of this. In Sec. 1.2 a cursory overview of the electronic structure theories is given and commonly used terminologies related to them are discussed.

1.2 Mean Field and Beyond

In this thesis, we deal with modeling electronic interactions beyond the mean-field by taking the mean-field function as a starting function. Hence, a clear understanding of the underlying mean-field model is crucial to our developments. The mean field wave-functions of the individual electrons (the orbitals!) are assembled as a *Slater determinant* to represent the many-particle state. The determinantal structure automatically takes care of the anti-symmetry and Pauli Exclusion Principle governing the wave function. However, there are a vast number of situations where a single determinant is inadequate for a proper description, be it to faithfully represent the spin-state of the function (an open shell singlet, for instance) or simply due to the near-degeneracy or *quasi-degeneracy* of a number of determinants such that the dominant determinant cannot be identified. A spin-adapted combination of determinants is called a Configuration State Function (CSF). A many-electron wave function which is a single determinant or a single CSF is said to be *single reference* (SR) while those which are a linear combination of several determinants or CSFs are said to be *multi-reference* (MR). A preliminary representation of an MR state is usually selected by first selecting a set of quasi-degenerate Slater determinants or CSFs. This set is called an "active space". A selection of quasi-degenerate functions is usually done by selecting certain "active" orbitals and "active" electrons and then distributing these active electrons in the active orbitals to generate the quasi-degenerate functions. When the active electrons are distributed in the active orbitals in all possible manner, a "complete active space" (CAS) is said to be generated. It may so happen, that some functions in this CAS are not quasi-degenerate with the others. If this is known, a judicious choice of active space may be made as a sub-set of the CAS. Such an active space is called an "incomplete model space" (IMS) in general. Several ways of systematically constructing specific IMSs have been proposed such as the Quasi-Complete and Isolated Incomplete Model Space (IIMS) of Kutzelnigg [11] and the Restricted Active Space (RAS) of Olsen et al. [12]. The zeroth order function is then, a linear combination of the active/model space functions. Denoting each model function of the N_d dimensional model space as ϕ_μ, the starting function for an MR theory may be written as:

$$\psi_{0k} = \sum_{\mu=1}^{N_d} \phi_\mu c_{\mu k}; \quad k = 1, N_d \tag{1.1}$$

Long-range, system-specific correlation due to near-degeneracy are called *non-dynamical/static correlation* while short-range correlation due to instantaneous electron-electron repulsions is called *dynamical correlation* [13]. The correlation energy usually refers only to the dynamical correlation and is defined as:

$$E_{correlation} = E_{exact} - E_{mean-field} \tag{1.2}$$

However, the two types of correlation are not mutually exclusive and a full inclusion of dynamical correlation within the limits of the basis set is essentially equivalent to the full inclusion of non-dynamical correlation and vice-versa.

For the purposes of this thesis, we would like to draw a distinction between the nature of the formal reference function (whether SR or MR) and the mean-field procedure by which the orbitals are obtained to construct the reference function. For example, orbitals obtained from an MR mean-field computation may be assembled as an SR function for further introduction of correlation. This would mean that the reference function is not the variationally optimized function for that state (it may not even be a physically meaningful state) but it may be a perfectly good reference function for the state we are interested in. However, one must be careful in reconstructing the Hamiltonian for the reference function and not assuming anything which follows from the variational optimization of the function. Alternatively, one may use orbitals from an SR mean-field optimization and construct the basis for the MR function. How the combining coefficients are obtained in this case depends on the nature of the correlation theory and we will come back to it later.

Starting from a mean-field SR theory (say, the Hartree-Fock theory [14, 15] (NR) or Dirac-Fock theory[16, 17] (Rel)) or MR theory (the Multi-Configuration Self-

Consistent Field theory (NR [18] or Rel [3, 19])), the electron correlation may be introduced in several ways viz. perturbative theories (PT), configuration interaction (CI), coupled cluster (CC), perturbative hierarchies for dynamical correlation like Algebraic Diagrammatic Construction (ADC) and other less organized hierarchies such as Coupled Electron Pair Approximation (CEPA), etc although the basic idea is to expand the functional space representing the wave function by mixing excited determinants/CSFs generated as a by-product of the mean-field procedure to introduce the effect of electron correlation. The former group of theories have both SR and MR versions. An extensive discussion on the varied aspects of electronic structure theory and the various methods for modeling electronic correlation may be found in the books by Helgaker et al.[10] and Yarkony (ed) [20]. Numerous reviews are also available [21, 22].

We may propose the problem in a second-quantized notation as follows:
Let, Ψ_0 be a starting mean-field function (SR or MR) and let us assume that there exists a *wave operator*, Ω, which acts on it to give the exact wave function, ψ.

$$|\psi\rangle = \Omega\,|\psi_0\rangle \tag{1.3}$$

Then the task set is to design an operator functional form for Ω (called Ansätz) and solve the SE to obtain its components. For PT, Ω is expanded as a perturbative series assuming electron correlation to be a perturbation to the mean-field model, CI adopts a linear Ansätz and CC uses an exponential Ansätz [23, 24, 25, 26, 27] (see Eq. (1.4)).

$$\begin{aligned} \Omega &= \sum_{i=0}^{\infty} \lambda^i \Omega^{(i)} \\ \Omega &= \sum_{l=0}^{n} c_l E_l \\ \Omega &= e^T \end{aligned} \tag{1.4}$$

where

$$\begin{aligned} T &= \sum_{l} t_l E_l \\ E_l\,|\psi_0\rangle &= |\chi_l\rangle \end{aligned} \tag{1.5}$$

In a given finite basis set, all full PT, CI and CC theories are exact and equivalent but the challenge lies in achieving the highest possible accuracy of the electronic energy at the lowest possible approximation. When the problem of incorporating correlation is tackled perturbatively giving the series of perturbative theories: MP2, MP3, etc. it is difficult to systematically approach the exact solution as this series converges very

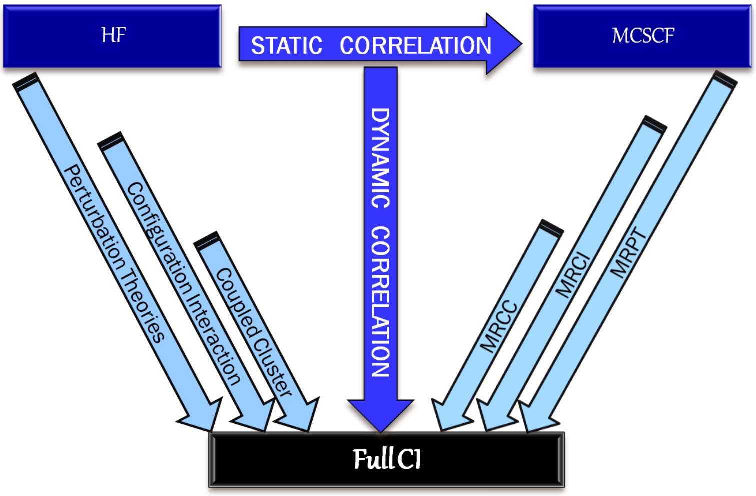

Figure 1.2: **Various hierarchies of theories for approaching the exact solution to the quantum many-electron problem**

slowly and not monotonically. CI has better success in terms of generating a converging series of theories but all approximate CIs fail in fulfilling the basic requirement of additive separability of energy in the non-interacting limit, ie. *size-consistency* (more in Sec. 1.3). In Fig. 1.2, the lengths of the arrows depict how far we have to go in the hierarchy to converge to the exact solution using the different types of methods. Coupled Cluster (CC) clearly scores on this ground. We shall see in Sec. 1.3 why the CC Ansätz is the natural choice for achieving size-consistency.

The relative benefits of a SR hierarchy vis a vis the MR hierarchy depends, of course, on the electronic state being studied. An MR state will approach the exact limit faster in an MR-based hierarchy while an SR state is better handled in an SR hierarchy. However, as is evident from Fig. 1.2, dynamical and non-dynamical correlation cannot be decoupled and usually influence each other.

The CC theory in the SR domain [28, 29, 30, 31, 32, 33] has proved its mettle over the last 50 years and is widely accepted as the best among the SR correlation theories. A similar universal-standard for MRCC theories is still elusive, the underlying reason being that MR electronic states themselves are of a wide variety and impose a number of stringent physical requirements on the theory which cannot all be met simultaneously as of now. The nature of these requirements and their implications on the formal structure of the theory are illustrated as and when they naturally arise. Several MRCC theories have been developed over the years and have shown promise within specific realms of applicability. The interested reader may look at the reviews by Lyakh et al. [34] and Köhn et al. [35]. This thesis continues the endeavors and aims at the formulation and implementation of a group of multi-reference coupled-cluster

(MRCC) theories which are designed to compute ionized and excited state energies per se (UGA-SUMRCC) or the energy differences directly (UGA-QFMRCC). We wish our theories to be spin-free and handle both complete and incomplete model spaces in a size-extensive manner. The strength of these theories lies in encompassing accurate prediction of not only the excitations and ionizations of valence electrons but also that of core electrons using the ground state orbitals in both cases which implies that the theories must have the capability of handling a high degree of orbital relaxation in the sense of Thouless' theorem [36]. Various intertwined issues need to be taken care of to accomplish this and we analyze them and suggest ways to circumvent the conceptual and technical bottlenecks as the thesis progresses.

1.3 *Connectivity, Size-extensivity and the Exponential Ansätz*

Size extensivity and size consistency are sometimes used interchangeably but they are, in a rigorous sense, quite different and must be carefully distinguished especially when we wish to use this as a basis for formulating a wave-function based electronic structure theory. Size extensivity [37, 38, 30] is the property of a theory to scale "properly" with the number of electrons. The word "properly" must be carefully considered. For any theory incorporating electron correlation, a linear scaling of the energy with the number of electrons is impossible. In general, the energy of a composite system, $A+B$, can be written as:

$$E_{A+B} = E_A + E_B + E_{AB} \tag{1.6}$$

Then, what is "proper" scaling ? The word "proper" may be interpreted as the absence of spurious interaction terms between the two sub-systems A and B such that if all the interaction terms between A and B (through the Hamiltonian) are switched off, E_{AB} becomes zero and $E_{A+B} = E_A + E_B$. For example, if a theory yields an energy expression of the form:

$$E_{AB} = g_A(p, q, ...)g_B(x, y, ...) \tag{1.7}$$

where $\{p, q, ...\} \cap \{x, y, ...\} = \{\}$, then even when all interaction between A and B is switched off E_{AB} will not go to zero. The parameters $p, q, ..., x, y, ...$ may be thought of as orbital labels in the context of electronic structure theories. Such a theory would be called size inextensive. However, if some theory has a form of energy as:

$$E_{AB} = g_A(p, q, .., i, ..)g_B(x, y, .., i, ..) \tag{1.8}$$

where $'i'$ is a common label in the sub-systems A and B, switching off the interactions would mean putting E_{AB} to zero. Such a theory would be called "size extensive" and the corresponding energy expression would be called "connected". It is this property of common labels or "connectivity" of energy expressions and all its components that will be utilized to analyze the size extensivity of any theories we put forward in the course of this discussion. Size consistency [29] on the other hand is the additive separability of the energy of two molecular fragments in the true dissociation limit. Thus, in a size consistent theory the energy of a homo-diatomic A_2 computed at large inter-atomic separation will be twice the energy of the atom A. The orbitals for the computation on A_2 are, in general, different from those for the computation on A but are related by some rotation. Thus, for a theory to be size consistent not only should the energy from it be size extensive in the sense that no spurious interaction terms are present but also invariant under rotation of orbitals.

Now, let us demand that any theory we formulate must have this property of separability of energy, ie. size extensivity. Let, the wave operator, Ω, transform the approximate wave function ϕ_0 to the exact function ψ_0.

$$\psi_0 = \Omega\phi_0 \tag{1.9}$$

Consider any partitioning of the system into sub-systems A and B. Then,

$$\phi_0 = \mathcal{A}[\phi_{0A}\phi_{0B}] \tag{1.10}$$

$$\psi_0 = \mathcal{A}[\psi_{0A}\psi_{0B}] \tag{1.11}$$

and we demand,

$$E_0 = E_A + E_B \tag{1.12}$$

when A and B are non-interacting. For an occupation number representation of the wave function, for example as:

$$\Omega = \sum_{ia} \Omega_i^a a_a^\dagger a_i + \frac{1}{2}\sum_{ijab} \Omega_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \tag{1.13}$$

the anti-symmetrizer, $\mathcal{A}$, is redundant as the creation-annihilation operators themselves subsume the property of anti-commutativity. Hence, we can write,

$$\psi_{0A} = \Omega_A\phi_{0A} \tag{1.14}$$

$$\psi_{0B} = \Omega_B\phi_{0B} \tag{1.15}$$

and hence,

$$\begin{aligned} \psi &= \psi_A \psi_B && (1.16) \\ \Omega \phi_{0A} \phi_{0B} &= \Omega_A \Omega_B \phi_{0A} \phi_{0B} && (1.17) \end{aligned}$$

Thus, the simple requirement for a size-extensive theory is that

$$\Omega = \Omega_A \Omega_B \tag{1.18}$$

An Ansätz which satisfies this requirement at any truncated level is:

$$\begin{aligned} \Omega &= e^T && (1.19) \\ \Omega_A \Omega_B &= e^{T_A} e^{T_B} && (1.20) \\ &= e^{T_A + T_B} && (1.21) \end{aligned}$$

In view of this insight, we change our idea of representing the wave operator as a linear combination of strings of creation-annihilation operators as in Eq. (1.13) to the exponential of an operator, T, which itself is a linear combination of strings of creation-annihilation operators. Thus, the CC Ansätz is naturally suggested by the requirement of size-consistency. For an MR situation, the CC Ansätz must be suitably modified keeping in mind the requirement of preserving the property of multiplicative separability of the wave operator in the non-interacting limit.

To begin to understand the world of multi-reference coupled-cluster (MRCC) theories one must start with understanding why the single-reference coupled-cluster (SRCC) is such a great success when it works and when it is that it doesn't. Thereon, we must pause to contemplate the following questions.

1) What desirable features of SRCC do we wish to preserve ?
2) What features of SRCC are in contradiction with its extension to MR situations (even if desirable) such that we cannot feasibly retain them ?
3) What additional properties must MRCC have in order to make it effective ?

1.4 SRCC: A Quick Visit

SRCC aims at incorporating electron correlation on top of a single-determinant SCF wave function, $|0\rangle$.It is a wave operator based approach which models the electron-electron interaction by means of an exponential Ansätz, e^T where T mixes virtual functions.

$$|\Psi_{CC}\rangle = e^T |0\rangle \tag{1.22}$$

The most common approximation is the Coupled-Cluster Singles Doubles (CCSD) theory [39, 40]:

$$|\Psi_{CCSD}\rangle = e^{T_1+T_2}|0\rangle \tag{1.23}$$

$$\equiv (1 + T_1 + T_2 + \frac{1}{2!}T_1^2 + \frac{1}{2!}T_2^2 + T_1T_2 + \frac{1}{3!}T_1^3 + \frac{1}{3!}T_2^3 + \frac{1}{2!}T_2T_1^2 + ...)|0\rangle \tag{1.24}$$

where T_1 and T_2 are the single and double excitation operators defined as:

$$T_1 = \sum_{i,a} t_i^a e_i^a \tag{1.25}$$

and

$$T_2 = \sum_{i,a,j,b} \frac{1}{2} t_{ij}^{ab} e_{ij}^{ab} \tag{1.26}$$

where i, j are the hole orbitals and a, b are the virtual orbitals. e_i^a and e_{ij}^{ab} are the elementary excitation operators whose structures in the second quantization notation are the following:

$$e_i^a = a_a^\dagger a_i \tag{1.27}$$

and

$$e_{ij}^{ab} = a_a^\dagger a_b^\dagger a_j a_i \tag{1.28}$$

t_i^a and t_{ij}^{ab} are the associated cluster amplitudes. A string of creation-annihilation operators is characterized by their order of action on a function. To make the order of action of the operators unique, a so-called "normal ordering" is defined. "Normal ordering" implies that all the annihilation operators in the string act before the creation operators. Normal ordering is always with respect to some function which is called the "vacuum". If the vacuum is the true vacuum (ie. an absence of particles), the strings which could generate a non-zero function would be strings of creation operators having a length equal to the number of particles in the system. This is unwieldy and hence, the vacuum chosen for correlation theories is generally the Hartree-Fock function which is called the "physical vacuum". Then, the T-operators acting on the Hartree-Fock function, ϕ_0, generate "excited functions" or "virtual functions" by annihilating particles from orbitals occupied in ϕ_0, ie. i,j,.. thereby creating "holes", and creating particles in the virtual orbitals, ie. a,b,.... All such excited determinants, along with $|0\rangle$, are said to span a Hilbert-space which forms the many-particle basis for a system with a fixed number of particles.

SRCC treats the leading contribution of pair-wise interaction to all orders through the exponentiation of the two-body operator T_2 while the orbital relaxation in presence of correlation is also modeled to all orders by the T_1 operator. The interpretation of the action of T_1 as modeling the effect of orbital-relaxation on energy follows from the Thouless theorem [36]. This feature of the SRCC Ansätz, e^T, to give importance to the most important physical interactions is responsible for the high accuracy of the SRCC energies. Triples, being computationally expensive, are sometimes included approximately on perturbative considerations giving rise to various theories such as CCSD-T [41], CCSD+T [42] and CCSD(T) [43, 44, 45, 46] among others. CCSD(T) is currently considered to be the *gold standard* of electronic correlation theories. The second implication of the exponential Ansätz is that it automatically ensures the product separability of the wave function in the non-interacting limit and hence, the additive separability of the energy, irrespective of the truncation of the T-operators at some n-body level. This is significantly different from a configuration interaction (CI) model which has this property of proper separability at full-CI level but loses it on truncation [47]. For a lucid exposition of SRCC, we would like to refer to the text by Crawford and Schaefer [48].

1.4.1 Limitations of SRCC

We have so far discussed the myriad advantages of SRCC. However, as soon as the applications were expanded to include more and more molecular states, several pitfalls were encountered. SRCC is not only size extensive, it is also orbital invariant. It will thus be size consistent as well if the underlying reference function correctly separates into fragments. However, the Hartree-Fock function, on which SRCC is based, does not behave correctly under fragmentation unless the fragments are all closed shell. Thus, in spite of having the redeeming features of size-extensivity and orbital invariance, size-consistency which is essential for computing potential energy surfaces (PES) is not achieved.

An issue we might pause to ponder here is: Is there any alternative choice of the starting function for an SRCC computation ? As a matter of fact, there are several alternatives [49] among which mention may be made of the "Brückner orbitals" [50, 51, 52] which are constructed so as to maximize the overlap, $\langle\psi_0|\phi_0\rangle$, between the starting function, ϕ_0 and the CC function, ψ_0. Such a construction, would result in all T_1s being zero. However, this construction implies knowledge of the CC function even before we have begun ! In practice, approximate conditions are used. The Brückner orbitals are useful only in very special cases where the CC function is of prime importance. The Hartree-Fock function always provides the best possible energy at the single determinant SCF level. The Brückner orbitals, however, are often good for properties other than energy [53] although they offer no advantage with regard to computing PES using SRCC.

The full SRCC, with any starting function, is, of course, an exact theory but like full-CI it is not practically viable. At the inception, it was believed that a singles-doubles or CCSD approximation would suffice as it modeled the two-body electron-electron interaction to all orders and this was definitely the most important correlation with three and higher body effects falling off rapidly. However, this is true only if the starting function is a reasonably good description of the wave function and it is only the electron-electron interaction which is missing. The dynamical correlation is modeled very effectively by SRCC but many molecular states require the inclusion of non-dynamical/static correlation which is nothing but an inadequacy of a single determinant to represent the wave function. This implies that the forced use of the Hartree-Fock function would result in a break-down of the underlying perturbative structure of the CC theory. The full SRCC theory would still produce the exact correlated function but the truncations cease to be physically motivated and systematic.

A hallmark of MR character is that certain T amplitudes for the SRCC become abnormally large. By the Brillouin condition of Hartree-Fock theory, the singly excited functions do not mix at first order which would mean that the T_1s are at least of 2nd order and should hence be small by perturbative arguments. If T_1 is large it indicates a failure of the perturbative argument. The T_1-diagnostic ($\sum\limits_{ia} t_i^a$), is thus considered a marker for MR character of a state although recent experience indicates that a combination of T_1-diagnostic and T_2-diagnostic may be a better indicator. As a consequence T_3s which should appear 3rd order onwards are also large and the minimal truncation for reasonably accurate SRCC energies appears to be CCSDT. The triples being computationally expensive are often taken partially on perturbative considerations [43, 44, 45, 46] but this is not enough to account for true MR character. Approaches involving inclusion of higher excitations such as T [54, 55] or Q [56] or their perturbative approximations [42] have been tried with mixed success and failure. Explorations using a selected subset of triples and quadruples involving the quasi-degenerate orbitals (the so-called CCSDt and CCSDtq methods) [57, 58, 59, 60, 61] which tries to map an MR description to an SR framework has also met with partial success. This is, however, expected as these are somewhat artificial approaches. A more physically motivated formulation would obviously be a CC based on a multi-determinant function, ie. an MRCC theory where the underlying perturbative assumptions would strictly hold.

1.5 MRCC: Possibilities and Pitfalls

Before we embark on the plethora of possible MRCCs, we repeat that it is essential to note that there are two possible reasons necessitating a multi-determinantal representation of the wave function. The first is the necessity for a solution of the Schrödinger equation with a spin-free Hamiltonian to be an eigenfunction of the S^2 operator which, in general, may not be possible with a single determinant. For example, an open-shell singlet or a triplet with $m_s = 0$ are necessarily combinations of two determinants. The second situation is when there exist a set of energetically close determinants which are said to be "quasi-degenerate" such that no function can be unambiguously given priority over the other as the zeroth order function. The term "multi-reference" is usually reserved for the latter case while theories dealing with the former are called "open shell CC" theories. Here it might be mentioned that the first MRCC theory by Mukherjee et al [62] is called open shell coupled cluster but it is truly a formalism for multi-reference coupled cluster.

The wave operator in an MRCC theory must act on ψ_{0k}, as defined in Eq. 1.1, to convert it to the exact function ψ_k. In principle, it is possible to generate N_d correlated wave functions starting from an N_d dimensional model space but it is not necessary that the chosen model space be a self-complete description for all k-roots. Thus, all k-roots may not be useful or well-described. At this point we are faced with several possibilities for the wave operator.

Option 1:

Ω can be designed to model only a specific state "k" such that only 1 root is targeted.

$$\psi_k = \Omega_k \psi_{0k} \tag{1.29}$$

Such an Ω is said to be state-specific and the corresponding MRCC is called "State-Specific MRCC" (SSMRCC) [63, 64, 65]. The details of Ω_k and the corresponding working equations offer several alternatives with their own advantages and disadvantages. At this point we do not enter into these details.

Option 2:

Ω may be parametrized so as to provide all N_d roots. Such an Ω will not have a k-dependence. When all the model functions belong to the same Hilbert space, ie. the function space for a fixed number of electrons, N, the corresponding MRCC is said to be a "State Universal MRCC" (SUMRCC) [66, 67] where,

$$\psi_k = \Omega \psi_{0k} \quad \forall\ k \tag{1.30}$$

Option 3:

Ω may be even further generalized to parametrize states of varying number of electrons. Here, the model functions are said to span a Fock space which is a function space for any number of electrons, n.

$$\psi_k^{(n)} = \Omega \psi_{0k}^{(n)} \quad \forall\ k, n \tag{1.31}$$

Note that Ω has no dependence on k or n. Hence, every parameter of Ω is computed once. Additional parameters may be computed for different k and/or n but no change in already computed parameters is necessary. Such an Ansätz yields what is called a "Valence Universal MRCC" (VUMRCC) [62, 68, 69]. A discussion of the essential aspects of VUMRCC relevant to this thesis is carried out in Appendix A.

Thus, the Ansätz gets more and more general from Option 1 through to Option 3. Historically, however, the development followed the reverse order from Option 3 (1975-78) [62, 68, 69] to Option 2 (1981) [66] to Option 1 (1997) [63, 64, 65]. In order to demonstrate why and how the scope of the most general VUMRCC Ansätz had to be narrowed we shall follow the historical route. We must mention, however, that, all three options have their own strengths and weaknesses and one or the other is most suitable for a certain type of application. There is, as of now, no "the" MRCC and one must make a judicious choice of which method to use based on the target applications. For example, while SSMRCC is most suitable for potential energy surfaces, VU and SUMRCC are more suitable for spectroscopic parameters like ionization potential, excitation energy, etc.

Moreover, as a subset of Option 2 or 3, it is possible to parametrize Ω for all N_d roots but only require that fewer roots $N_p (N_p < N_d)$ which are not prone to intruders (See Appendix B) are eigenvalues of H thereby bypassing numerical instabilities as well as deterioration of targeted roots through unnecessary coupling with poorly described roots. These are called the Intermediate Hamiltonian theories which were originally proposed by Kirtman [70] and expanded by Malrieu et.al. [71, 72] but were not size-extensive. Later developments by Mukherjee [73, 74, 75], Malrieu [76, 77, 78, 79] and others [80, 81, 82, 83] lead to size-extensive formulations.

We should most definitely mention that the enlistment of the three options above is by no means exhaustive. These are the three main routes that can be adopted but hybrid methods such as "Quasi-Fock" or "Quasi-Hilbert" also exist [84, 85, 86] and may be more suitable alternatives for some problems of interest.

1.5.1 MRCCs in Fock-space

VUMRCC [62, 68, 69] is well-suited to computation of energy differences especially between states with varying number of electrons, eg. ionization potentials and electron affinities. The theory exploits the fact that the wave function in occupation number representation only depends on orbitals and not on the number of electrons. Thus conceiving Ω as in Eq.1.32 to be independent of k and n (viz. Eq. (1.31)) is perfectly valid.

$$\Omega = e^{T} \tag{1.32}$$

Moreover, the Subsystem Embedding Condition (SEC) (see Appendix A) allows a clean identification and separation of lower valence sector energies in the higher valence sector expressions thereby allowing us to analytically drop the energy of the state with respect to which we require the energy difference. This improves the accuracy as common terms exactly cancel and the theory models the energy difference directly. VUMRCC has achieved much success in the determination of ionization potentials, electron affinities and excitation energies.

The construction of PES using VUMRCC is, however, fret with difficulties arising from the so-called "Intruder Problem" [87, 88] which is discussed in Appendix B. In some specific cases the problem may be alleviated by using an IMS [89] but this requires a consideration of the normalization of Ω for maintaining size-extensivity [90, 11, 91, 92] which is discussed in Appendix C and Sec. 2.1.3.

A very clean way of alleviating the intruder problem in VUMRCC is by casting the equations as a matrix eigenvalue problem. Two paths are available for casting a non-linear set of equations into a matrix eigenvalue problem. The first is the "Eigenvalue Dependent Partitioning" of Löwdin [93, 94] and the second is the "Eigenvalue Independent Partitioning" which was proposed for VUMRCC by Mukherjee [73]. This method combines the advantages of a CI-like solution strategy with the accuracy and size extensivity of an MRCC.

The linear response theory (LRT) approach is a general framework for response properties of a wave function. This class of theories for computation of energies may be perceived as a subset of the VUMRCC theory. The CC-LRT [95, 96, 97, 98] has been widely applied to the computation of excitation energies and properties at the CC level. One of the simplest applications is, of course, the determination of differences of state energies as poles of the linear response function. This particular response equation for energy differences can be recast as the Equation-Of-Motion CC (EOM-CC) equation [99, 100, 101, 22] (see Appendix F). A very similar but independently developed formalism called Symmetry Adapted Cluster Configuration Interaction (SAC-CI) was proposed by Nakatsuji [102, 103]. The CC-LR [95, 96, 97, 98], SAC-CI [102, 103] and EOMCC [99, 100, 101, 22] approaches are conceptually and structurally very similar and may be generically known as SRCC based linear response theories (SR-LR). These methods mainly differ in their computation of transition probabilities connecting the ground and the excited/ionized states. Common characteristic features of all SR-LR theories are: (a) they assume single reference character of the GS and (b) the methods are core extensive only unlike the VUMRCC which is fully extensive. Linear Response theories with an MR starting function, the MR-LRT

[104, 105] and MR Equation of Motion (MREOM) approaches [106, 107, 108, 109, 110] have also been developed. A related theory, somewhat in-between a full VUMRCC and an EOM approach is the STEOM-CC of Nooijen and Bartlett [111, 112, 113] which can also handle the excited/ionized states size extensively but differs in the details of implementation from VUMRCC.

The problem with VUMRCC is that it generates much more information than we need making it all the more prone to problems which may have no bearing on the state of interest but would prevent us from computing it. In view of the intruder problem and SEC the generation or requirement for too much information is often more of a curse than a blessing in spite of the generality and elegance of the formulation.

1.5.2 MRCCs in Hilbert Space

A somewhat more intuitive approach is to only consider a Hilbert space of many-electron functions for a fixed number of electrons. This was first suggested by Jeziorski and Monkhorst [66] who used a multi-exponential wave operator Ansätz defined in Eq.1.33, now commonly known as the Jeziorski-Monkhorst (JM) Ansätz.

$$\psi_k = \Omega\psi_{0k} = \sum_{\mu=1}^{N_d} e^{T_\mu} \left|\phi_\mu\right\rangle c_{\mu k} \tag{1.33}$$

When this Ansätz is used in the Schrödinger equation to solve for all N_d roots, the resulting theories are called SUMRCC theories while a solution for one root results in an SSMRCC theory.

A middle path between VUMRCC and the SUMRCC may be adopted leading to the so-called Quasi-Fock and Quasi-Hilbert space theories [84, 85, 86] which enables the direct computation of energy differences between states of same or different electron number without the need to go through all intermediate valence sectors. Such approaches have been found to be useful especially for the computation of excitation energies without the need to compute the ionization potentials (IP) and electron affinities (EA).

The strength of the JM Ansätz may be perceived through the following consideration. We have so far discussed Ansätze where the excitation operators are always defined with respect to a single closed shell function (say, having N electrons) which may or may not feature in the model space for the target functions and bear only orbital labels. Let us consider a situation where we have two model functions, ϕ_μ and ϕ_ν having N-1 electrons:

$$|\phi_\mu\rangle = a_u|\phi_0\rangle \tag{1.34}$$

$$|\phi_\nu\rangle = a_v|\phi_0\rangle \tag{1.35}$$

Excitations, say, T_i^a, should have different amplitudes for the two model functions. In the case of any valence-universal Ansätz, as discussed above, the difference is ensured by certain spectator containing operators of higher rank, for example, T_{iu}^{au} for ϕ_μ and T_{iv}^{av} for ϕ_ν. However, with increase in active orbital occupancy, the rank of the operators keep increasing making it impractical. The JM Ansätz is much more compact as it simply introduces a model function dependence on the T-amplitudes.

The normal ordering of the T-operators defined in terms of spinorbitals was conceived by Jeziorski and Monkhorst [66] to be with respect to the corresponding model functions. Thus, the T_μs commute with each other but not with the T_νs. When this Ansätz is used in a state-universal context as in Eq. (1.30) there are as many equations as there are unknowns and there is hence, no redundancy. However, when it is used in the state-specific context as in Eq. (1.29) there are less equations than there are unknowns necessitating the use of sufficiency conditions to solve the equations. The choice of these sufficiency conditions is guided by considerations of size extensivity, avoidance of intruders and a correct perturbative structure. The SSMRCC proposed by Mukherjee (called Mk-MRCC) satisfies all three criteria. The BW-MRCC, developed by Mášik and Hubač [114] uses a different sufficiency leading to a size-inextensive SSMRCC but this is free of intruders as long as the energies of the virtual functions are well separated from the target energy of the system. This was further extended by Pittner et al. who attempted to restore size-extensivity [115, 116, 117] but this resulted in a resurfacing of the intruder-problem. A Coupled Electron Pair Approximation (CEPA)-like formalism was developed by Malrieu et al. [118] where a suitable 'dressing' of an MRCISD matrix leads to the elimination of the size-inextensive terms. This has a deep structural resemblance to the CEPA variant of the Mk-MRCC [119, 120] but cannot be easily extended to the full CC theory, presumably because it starts from a formulation which is inherently quasi-linearized. In the MRexpT theory of Hanrath [121, 122, 123], the redundancy problem is side-stepped by an 'anonymous parentage approximation' for the t-amplitudes leading to only a core-extensive theory but with reasonably good accuracy. Approaches involving the use of reference-independent inactive cluster amplitudes [124, 125] are useful on grounds of computational efficacy but since, the inactive cluster amplitudes are non-redundant, the problem of redundancy of the other amplitudes remains.

The JM Ansätz suffers from two major difficulties. The first is the lack of invariance of the energy under rotation of orbitals making it size-inconsistent in general. The use of localized orbitals can give size consistent behavior [126] but restoring orbital invariance in the JM Ansätz seems difficult. The second is the lack of "complete coupling" [123, 127] between the excited space functions. By this we mean that under a given truncation scheme of the T operators, not all model functions are treated on the same footing. For example, in a CCSD truncation scheme, an excited function, χ_l, may be reachable from ϕ_μ by a T_2 but can be reached from ϕ_ν only by a T_3 which is absent in our scheme of things. Thus, the coupling of ϕ_μ and ϕ_ν via χ_l is incomplete. In strongly multireference situations this has been shown to play a very important role [128].

Another aspect of the spinorbital-based JM Ansätz is the spin contamination which is characteristic of any spinorbital-based non-linear Ansätz. Even if the T-operators in spinorbital basis are adapted to a particular spin (non-singlet), their powers are not. To solve this problem, we have introduced a modified JM Ansätz which is unitary group adapted, leading to the UGA-SUMRCC [129], UGA-QFMRCC [130] and UGA-SSMRCC [131]. The first two theories have been discussed in detail in the subsequent chapters and form the focus of this thesis. UGA-SSMRCC is closely related and references will be made to it when applicable. These MRCCs using the JM Ansätz constitute the class of *Decontracted MRCC* theories. This class of theories is generically plagued by the problem of redundancy of cluster amplitudes and the lack of invariance of the energy with respect to rotation of active orbitals. Both these problems stem from the model-function dependence of the cluster amplitudes and hence, are inherent to the JM Ansätz. Being an effective Hamiltonian theory, SUMRCC suffers from the intruder problem making it difficult to use it for constructing PES. Efforts to alleviate this problem by using incomplete model spaces have been explored with mixed success and failure [132, 133, 134]. However, it is well-suited for computation of energies and properties at equilibrium whether with a CAS or an IMS [67, 135]. The state-specific theories are, on the other hand, geared towards computation of PES.

For completeness, we should mention that a second approach is possible for construction of an SSMRCC, viz. use of a single exponential Ansätz acting on a combination of the model functions (see Eq. (1.36)). This class is constituted by the *Contracted MRCC* theories. This class of theories has the potential to overcome both the problems mentioned in the previous para. However, the definition of T-operators for an MR function and the subsequent theoretical considerations presents a new set of challenges.

The Ansätz for an internally contracted CC function, originally proposed by Banerjee and Simons [136, 137] can be written as:

$$|\psi_k\rangle = \Omega\,|\psi_k\rangle = e^T \sum_\mu |\phi_\mu\rangle\, c_{\mu k}. \tag{1.36}$$

However, they overlooked the importance of selecting a linearly independent manifold of excitation operators and also discarded some physically important classes of T-operators leading to a somewhat incomplete theory. The first complete MRCC theory using this Ansätz was developed by Mukherjee [138, 139] and Mukherjee et al. [64] and was named the Internally Contracted Multi-Reference Coupled Cluster (ICMRCC) theory. This theory required the use of the concept of a 'Generalized Normal Ordering' (GNO) [138, 139] which is a normal ordering with respect to an MR function such that the expectation value of the normal-ordered operator for the reference MR function is zero. Further work was carried out by Evangelista et al. [140, 141] as well Hanauer and Köhn [142]. The issue of size-extensivity proved tricky and elusive but was finally resolved by very careful analysis of the working equations and was found to be crucially dependent on the use of the GNO for the T-operators as also the scheme for selecting the manifold of linearly independent T-operators [143]. A spin-adapted ICMRCC, the UGA-ICMRCC, has also been recently proposed from our group [144]. Unlike in the internally contracted MRCI approaches [145, 146], the combining coefficients, $c_{\mu k}$, are not fixed at a pre-determined value but can be obtained self-consistently in presence of electron correlation. Consequently, the manifold of linearly independent T-operators can also not be predetermined.

1.6 Spin Adaptation of the CC Ansätz

An eigenfunction of a spin-free Hamiltonian ought to be an eigenfunction of the S^2 operator. While richer Hamiltonians with relativistic terms do not have this requirement, a breakdown of the spin eigenfunction nature of the wave-function while using a spin-free Hamiltonian must be an artifact arising from an erroneous treatment of the problem. It is well documented that spin contamination plays a rather significant role in the loss of accuracy of state energies and that it plays a vital role in the computed properties of molecules. Thus, spin adaptation of a many-body wave-function has been the subject of much research with the focus not only on spin adaptation as such but also on a workable scheme for actual computation.

In correspondence with the Pauli exclusion principle, a many-electron wave-function is anti-symmetric under both exchange of space-spin coordinates of electrons and interchange of the spinorbitals comprising it. Of course, the simplest of such functions is a Slater determinant. This satisfies the Pauli principle, but - except for special situations - is not an eigenfunction of S^2. This leads to a bigger dimension of the Hilbert space for the matrix of the Hamiltonian, which in some anti-symmetric functions with a fixed spin would have led to a block-diagonal form corresponding to each value of the spin. The simplest of such functions consists of a spacial function, ψ, and a spin function, Σ, and is known as a configuration state function (CSF). A CSF can be denoted by a generic function, Ψ:

$$\Psi = \mathcal{A}\psi\Sigma \tag{1.37}$$

Moreover, since the NR Hamiltonian does not affect the spin part of the wave-function, the Schrödinger equation indicates that the wave-function, Ψ, in an NR situation can be factorized into a spatial part, ψ and a spin part, Σ.

$$\Psi = \psi\Sigma \tag{1.38}$$

where the overall anti-symmetry of Ψ is ensured by choosing ψ and Σ belonging to adjoint irreducible representations (IRREPs) of whatever group is used for spin adaptation. The most obvious scheme for spin adaptation of the full wave-function is thus, to simply augment ψ with a Σ of a given spin. At this point, it becomes important to realize that S^2 has degenerate sets of eigenfunctions making the selection of Σ non-unique. One might also wish that the functions selected with the same S^2 value are orthogonal to each other. Keeping the desire for orthogonality in mind, one option is to use Clebsch-Gordon coefficients from the SU2 group, wherein different functions with the same S^2 value, but different spin-coupling schemes, transform as bases for different IRREPs. Here, the basis functions for a given IRREP form an orthonormal set, and additionally the basis functions belonging to different IRREPs are also orthogonal. Several interrelated spin-coupling schemes exist in the literature and a comprehensive review may be found in the books by Pauncz [147, 148]. If we relax the requirement of orthogonality, valence bond functions may also be brought within this ambit. A second option is to use the fact that the indistinguishability of electrons implies that an N-electron wave-function belongs to the symmetric group (also called permutation group, S_N). It can be shown by the Dirac identity that the permutation and spin operators are related [148]. Thus, in order to obtain a spin adapted Ψ, we may exploit the equivalence of using the spin-symmetry of Σ via the SU2 group (first option) and the permutational symmetry of ψ employing the symmetric group S_N and obtain a spin-free formalism such as that of Matsen [149]. The spin-part of the wave-function is entirely determined by the adjoint of the IRREP of S_N to which the spatial part belongs. Both these approaches get more and more complicated with increasing number of electrons and the handling of the coupling co-efficients whether from the spin-coupling schemes or the S_N group becomes computationally inefficient.

A third, and till date the most promising, approach is to use another symmetry of the many-electron wave-function – its anti-symmetry under interchange of spinorbitals. An interchange of spinorbitals amounts to a special unitary transformation of the spinorbital basis and hence an N-electron wave-function belongs to the anti-symmetric IRREP of the unitary group, U(2N). It was shown by Paldus, inspired by the works of Moshinsky [150] in nuclear physics, that to express any spin-independent particle number conserving operator in terms of generators of the unitary group, such as the non-relativistic Hamiltonian, it is only necessary to use the sub-group U(N) thereby obtaining a factorized representation in the IRREPS of $U(2N) \supset U(N) \times U(2)$ for the full Ψ. A comprehensive exposition of the use of the unitary group for spin-adapting wave-functions and its relationship with the other two approaches, viz. the SU2 and S_N groups can be obtained in the book edited by Hinze [151]. The most prominent advantage of the unitary group is that a very efficient method is available for the evaluation of matrix elements of generators of the unitary group between functions belonging to two IRREPs of U(N) by representing the bra and ket functions graphically, as shown by Shavitt [152, 153], and this facilitates such evaluations enormously. This transcription is known as the Graphical Unitary Group Approach (GUGA) [152, 153].

A major challenge for treating open shell and multi-reference systems (whether SR or MR) at the coupled cluster level is the spin adaptation of the wave function when it is parametrized by a non-linear Ansätz. For single determinant open shell states one usually adopts a spin-orbital based theory to achieve natural termination at the quartic level and it is well known that this leads to spin-broken solutions [154, 155, 156, 157]. The spin adaptation of the CC Ansätz in the SR domain has been and still is a subject of active research [158, 45, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170]. For SRCC formulations using spinorbitals based on a high spin single determinant, a spin restricted formulation [167] satisfying the constraint of preserving the expectation value of S^2 and a spin adapted formulation [169] forcing the eigenfunction nature of the coupled cluster function with respect to S^2 were suggested but lead to rather unwieldy working equations for the cluster amplitudes. These days, for SRCC formulations for non-singlet cases, the spin contamination arising out of a spinorbital based formulation is tolerated, mostly for reasons of simplicity [154, 156].

The unitary group gave a fresh impetus to these efforts. A significant step forward was accomplished by Jansen and Schaefer [159] who used generators of the unitary group to define spin-free cluster operators for high spin single reference non-singlet states. A more compact and elegant formulation along a similar vein was put forward by Li and Paldus [162, 171] for a single configuration state function (CSF) as the reference. Some detailed Lie algebraic aspects of the unitary group adapted (UGA) SRCC, based on one CSF were also analyzed by Jeziorski, Paldus and Jankowski [172]. Li and Paldus have extensively worked on several aspects of UGA theories [173, 162, 174, 165, 175, 176, 177, 178]. As we shall discuss in greater detail later (Chp. 2), the use of spin-free generators necessarily introduces non-commuting excitation operators rendering the Baker-Campbell-Hausdorff (BCH) expansion non-terminating.

Clearly, one needs to abandon the exponential parameterization for ensuring a spin-free formulation while ensuring the termination of the coupled cluster equations at the quartic power.

At the MRCC level, the degree of difficulty of spin adaptation depends on the class of MRCC theory one wants to adapt to the proper spin. Among the three major approaches to MRCC, namely, valence universal (VUMRCC or FS-MRCC) [62, 68, 69], state universal (SUMRCC) [66] and state specific (SSMRCC) [63, 64, 65], only the VUMRCC is inherently spin adapted. On the other hand, the Jeziorski-Monkhorst (JM) Ansätz [66] used in the last two types of MRCC theories, is not inherently spin adapted and in a truncated coupled-cluster scheme results in spin broken solutions for non-singlet states. The spin adaptation of the JM Ansätz has received considerable attention, concurrently with the spin adaptation of the SRCC function for open-shell states [179, 180, 162, 164, 181, 182, 131, 129, 130, 183].

The most recent endeavor in this direction has been the use of the normal ordered JM-like Ansätz with cluster operators defined in terms of generators of the unitary group, first introduced by Maitra et.al. [131] in the context of the so-called UGA-SSMRCC. The model functions in this approach are Gel'fand adapted and to indicate this the method was termed as a Unitary Group Adapted SSMRCC (UGA-SSMRCC) theory. It combines the twin advantages of the avoidance of spin contamination and a natural termination of the so-called 'direct' term at the quartic power of the working equations of the SSMRCC theory. In this thesis, following an early lead by Mukherjee and Zaitseveskii [184] we are led to the same Ansätz to formulate a UGA-SUMRCC [129] theory which also shares the desirable properties of absence of spin contamination as well as termination of the direct term at the quartic power. We should mention here that, another spin-free generalization of the JM Ansätz using generators of the unitary group was suggested by Datta and Mukherjee known as the Combinatoric Open-Shell SUMRCC (COS-SUMRCC) [181] and the COS-SSMRCC [182], which is structurally closer to the parent spin-orbital based JM Ansätz and is thus probably the closest spin-free analogue of JM based MRCC theories. The applications thereof [181, 182, 185] are still confined to one valence problems, although generalization to encompass multi-valence situations are expected to indicate the potentiality of the approach. As things are at present, the UGA-based SU and SSMRCC [131, 125, 129, 130] appear to be simpler alternatives.

1.7 Scope of the Thesis

We want to present in this thesis a general spin free approach for computation of excited or ionized state energies. The state universal framework is chosen for our developments and the unitary group approach is used to spin-adapt the non-linear

JM Ansätz leading to the Unitary Group Adapted State Universal MRCC (UGA-SUMRCC). A related Ansätz is used to formulate a theory allowing direct computation of energy differences between a closed shell ground state and an excited or ionized state leading to what we call the Unitary Group Adapted Quasi-Fock MRCC (UGA-QFMRCC). Our efforts in UGA-QFMRCC are directed towards the formulation of a theory for calculation of direct energy difference for the target sector with respect to the GS *without going through intermediate valence sectors*. Thus, in our strategy, the computation of excitation energy does not involve a prior computation of ionization energy and electron affinity. For both theories, the formulations consider the possibility of using IMSs in general and intermediate normalization has not been assumed in order to prevent loss of size extensivity. We have also formulated the analytic gradients for the single CSF limit of UGA-SUMRCC which we call the Unitary Group Adapted Open-Shell Coupled Cluster (UGA-OSCC) theory. To indicate the accuracy to be expected from it we have carried out some representative computations of low order electric properties viz, dipole moment and polarizability of a set of neutral radicals using the numerical gradient technique.

In this thesis we will not only formulate the UGA-SUMRCC and UGA-QFMRCC theories for both complete and incomplete model spaces and benchmark them but also explore several aspects of the theories:

(i) The first issue pertains to analyzing our choice of cluster operators vis-a-vis those used by Li and Paldus [162] to formulate SUMRCC in a UGA framework. In particular we will show that suitable linearly independent cluster operators can be discerned from simple perturbative reasoning although they will no longer lead to orthogonal excited functions. In effect, for singles-doubles truncation scheme the combination appears to be the same using the perturbative analysis in comparison with explicit SU2 adaptation. One avenue which we shall look into is the possibility of deliberately using certain redundant cluster operators and concomitantly using suitable sufficiency conditions to supply the working equations. We carry out comparative studies of projection equations with linearly independent operators against the use of sufficiency conditions with a linearly dependent manifold. An alternative path of using amplitude equations instead of the projection equations is also explored.

(ii) We shall also try to assess the extent of orbital relaxation and correlation relaxation effects achievable through our parametrization vis a vis a Fock-space like approach at one end and a COS-CC approach on the other. This study is undertaken in the context of core electron ionization and excitation where these effects are largest.

(iii) The third issue we will look into is to assess the performance of the UGA-SUMRCC for state energy against the UGA-QFMRCC.

(iv) We will also discuss in detail several aspects of connectivity and size extensivity of the parent UGA-SUMRCC and the consequent size intensivity of the excitation energies from UGA-QFMRCC. The occurrence of reduced density matrices in the working equations introduces several non-trivial aspects into the proof of size-extensivity and we discuss why and how the issues of connectivity of operators and extensivity of the amplitudes must be carefully distinguished in general. A study of the performance of all our proposed variants across a chosen set of small molecules is undertaken. We try to assess the trends in energies computed using UGA-SUMRCC and its approximants along a series of bases of increasing size. Statistical data in a reasonable sample space is provided for a more objective analysis.

We have partitioned the rest of this thesis into four major chapters. Chap. 2 deals with the formulation and exploration of the UGA-SUMRCC and UGA-QFMRCC in all its forms. Chap. 3 discusses the aspect of orbital relaxation built into our formalisms in the context of ionization and excitation of electrons especially the core electrons. The role of scalar relativistic effects in the ionization of core electrons from medium-heavy atomic centers is also studied. In Chap. 4 we develop the analytic gradients for computation of molecular properties using the UGA-OSCC formalism and compute dipole moments and polarizabilities via the numerical gradients of UGA-OSCC. In the next chapter, Chap. 5, the non-trivial algorithmic aspects of our suite of UGA-MRCC theories and their gradients is discussed along with details of implementation. We conclude in Chap. 6 with a summary of the thesis and a brief outlook on future avenues of development which we wish to explore.

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Chapter 2

Theoretical Development of Spin-Free Multi-Reference Coupled Cluster Theories with Applications to Ionization and Excitation Energies

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2.1 Formulation of the Theories

In this chapter, we develop two spin-free MRCC theories for computing ionization and excitation energies. The first approach involves computation of the energy of the ionized/ excited state in a state-universal context, called the Unitary Group Adapted State Universal MRCC (UGA-SUMRCC) (see Sec. 2.1.1). The second approach is a spin-free valence-specific formulation for direct energy differences with respect to a closed shell ground state, which we call Unitary Group Adapted Quasi-Fock MRCC (UGA-QFMRCC) (see Sec. 2.1.2). Both these approaches share the advantages of being capable of handling open shell ionized and excited states without spin contamination, while maintaining the natural truncation of the direct term and hence, the ease of implementation. The theories are manifestly size-extensive and the modifications for using incomplete model spaces (IMS) without losing this feature are also discussed.

2.1.1 UGA-SUMRCC

The original spinorbital-based JM ansatz for Ω for the various states ψ_k, where

$$\psi_k = \Omega\psi_{0k} \tag{2.1}$$

and

$$\psi_{0k} = \sum_{\mu} \phi_\mu c_\mu \tag{2.2}$$

is given by:

$$\Omega = \sum_{\mu} \Omega_\mu |\phi_\mu\rangle\langle\phi_\mu| \tag{2.3}$$

with

$$\Omega_\mu = e^{T_\mu} \tag{2.4}$$

As discussed in Chap. 1, this set of T_μ operators are normal-ordered with respect to ϕ_μ and hence, commute with each other although they do not commute with the operators T_ν of any other model function ϕ_ν.

A re-definition of the T-operators as generators of the unitary group in order to obtain a spin-free theory with a non-linear Ansätz simply means that the operators accompanying the cluster amplitudes are now expressed as spin-summed strings of creation and annihilation operators. This is equivalent to considering the cluster operators to be labeled by spatial orbitals. The representation of the T-operators using spin-free excitation operators makes the Ts non-commuting as the singly occupied orbital labels occur both as creation and annihilation operators. We thus introduce a normal ordering, {...}, of the exponential Ansätz which operationally reinstates this commutativity and plays a vital role in making this theory amenable to implementation for arbitrary valence sectors and active spaces. The spin-free analogue of the JM Ansätz for Ω_μ which we propose to use in this thesis is thus:

$$\Omega_\mu = \{e^{T_\mu}\}. \tag{2.5}$$

The curly bracket above indicates normal ordering with respect to a suitable closed shell vacuum $|0\rangle$. The state $|0\rangle$ is taken in UGA-SUMRCC theory to be the closed shell ‘core‘ determinant containing doubly occupied inactive orbitals common to all the ϕ_μs. For example, we will choose our vacuum, $|0\rangle$, as the HF ground state of the system for excited and ionized states dominated, respectively, by h-p and 1h/1p functions relative to it. The ϕ_μs are unitary group adapted Gel’fand Configuration State Functions (CSF) [1] generated from the vacuum state $|0\rangle$ by unitary group adapted Gel’fand creators. We use the Graphical Unitary Group Approach of Shavitt [2, 3] to construct matrix elements between these Gel’fand CSFs. The excited states in our formulation are generated by the action of spin-free generators of the unitary group ($\{\epsilon^l_\mu\}$), acting on ϕ_μ:

$$|\chi^l_\mu\rangle = \{\epsilon^l_\mu\}|\phi_\mu\rangle \tag{2.6}$$

where $\{\epsilon^l_\mu\}$ are in normal order with respect to $|0\rangle$. The functions χ^l_μ are CSFs but they are neither Gel‘fand states nor the SU2 adapted CSFs of Li and Paldus [4]. $\{\epsilon^l_\mu\}$s are linearly independent specific combinations of spatial orbital replacement operators, $\{E^l_\mu\}$, which are generators of the unitary group. The final working equations involve matrix elements between ϕ_μs wherein reduced density matrices (RDM) appear which incorporate the spin information of the target state and hence how we choose the excited CSFs do not play an important role.

Using this new Ansätz in the Schrödinger equation we are led to the following equations:

$$\begin{aligned}
H\,|\psi_k\rangle &= E_k\,|\psi_k\rangle \quad \forall \quad k \\
\{H\}\sum_\mu \{e^{T_\mu}\}\,|\phi_\mu\rangle\, c_{\mu k} &= E_k \sum_\mu \{e^{T_\mu}\}\,|\phi_\mu\rangle\, c_{\mu k} \\
\sum_\mu \{e^{T_\mu}\overline{H}_\mu\}|\phi_\mu\rangle c_{\mu k} &= \sum_{\mu\nu} \{e^{T_\nu}\overbracket{e^{T_\nu} W_{\nu\mu}}\}|\phi_\mu\rangle c_{\mu k} \\
\sum_\mu \{e^{T_\mu}\overline{H}_\mu\}|\phi_\mu\rangle c_{\mu k} &= \sum_{\mu\nu} \{e^{T_\mu}e^{-T_\mu}e^{T_\nu}\overbracket{e^{T_\nu} W_{\nu\mu}}\}|\phi_\mu\rangle c_{\mu k} \\
\sum_\mu \{e^{T_\mu}\overline{H}_\mu\}|\phi_\mu\rangle c_{\mu k} &= \sum_{\mu\nu} \{e^{T_\mu}Y_{\nu\mu}\}|\phi_\mu\rangle c_{\mu k}
\end{aligned} \tag{2.7}$$

where

$$\overline{H}_\mu = \overbracket{He^{T_\mu}} \tag{2.8}$$

is a compact notation of the series:

$$\overline{H}_\mu = \{H\} + \{\overbracket{HT_\mu}\} + \frac{1}{2}\{\overbracket{\overbracket{HT}_\mu T_\mu}\} + ... \tag{2.9}$$

and

$$Y_{\nu\mu} = e^{-T_\mu} e^{T_\nu} \overbracket{e^{T_\nu} W_{\nu\mu}} \tag{2.10}$$

The 'contraction', $\overbracket{AB}$, connecting two strings of operators A and B denotes sum of all possible contractions involving all pairs of operators from both A and B. Terms like $\{\overbracket{\overbracket{HT}_\mu T_\mu}\}$, etc. involve contractions between H and the various T_μs excluding contractions between the operators of different T_μs. The operator, $W_{\nu\mu}$, is a closed operator labeled by orbitals distinguishing ϕ_μ and ϕ_ν. It transforms ϕ_μ to ϕ_ν via the relation:

$$W_{\nu\mu}|\phi_\mu\rangle = |\phi_\nu\rangle\langle\phi_\nu|H_{eff}|\phi_\mu\rangle \tag{2.11}$$

It is composed of operators of various ranks, the lowest rank being the number of orbitals by which μ and ν differ. $W_{\nu\mu}$ may also contain components with any number of spectator scatterings involving creation and destruction of common active orbitals of ϕ_μ and ϕ_ν, resulting in the ranks of the operator being higher. The spectators need not all be diagonal, it is only essential for the group of destruction operators to be the same as the group of creation operators, the labels being that of the common orbitals of μ and ν.

Applying Wicks' theorem in reverse on the LHS of Eq. 2.7 successively, we get,

$$\begin{aligned} LHS &= \sum_\mu [\{e^{T_\mu}\}\{\overline{H}_\mu\} - \{e^{T_\mu}\overbracket{e^{T_\mu}\overline{H}_\mu}\}]|\phi_\mu\rangle c_{\mu k} && (2.12) \\ &= \sum_\mu [\{e^{T_\mu}\}\{\overline{H}_\mu\} - \{e^{T_\mu}\}\{\overbracket{e^{T_\mu}\overline{H}_\mu}\} + \{e^{T_\mu}\ \overbracket{e^{T_\mu}\overbracket{e^{T_\mu}\overline{H}}_\mu}\}]|\phi_\mu\rangle c_{\mu k} && (2.13) \end{aligned}$$

We can factorize $\{e^{T_\mu}\}$ by further iterating the factorization in Eq. 2.13

This can go on generation by generation depending on the number of active destructions possible. To use a compact notation we can denote this chain as:

$$\begin{aligned} LHS &= \sum_{\mu}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}\overline{H}_\mu}\}]|\phi_\mu\rangle c_{\mu k} && (2.14)\\ &= \sum_{\mu}[\{e^{T_\mu}\}\{X_\mu\}]|\phi_\mu\rangle c_{\mu k} && (2.15)\end{aligned}$$

where,

$$\{e^{\theta}\} = \{1 - T_\mu + \overbracket{T_\mu T_\mu} + \frac{1}{2!}T_\mu T_\mu - \frac{1}{2!}T_\mu \overbracket{T_\mu T_\mu} - \frac{1}{2!}\overbracket{T_\mu T_\mu} T_\mu + \frac{1}{2!}\overbracket{T_\mu T_\mu}\,\overbracket{T_\mu T_\mu} - ...\} \quad (2.16)$$

with

$$\theta = \{-T_\mu + \overbracket{T_\mu T_\mu} - ...\} \quad (2.17)$$

and $\{\overbracket{e^{\theta}\overline{H}_\mu}\}$ has been denoted as $\{X_\mu\}$ in Eq.2.13 . The structure of the connected composite θ in Eq. 2.17 and the representation of the sum of all composites in $\{X_\mu\}$ as $\{e^{\theta}\}$ connected to $\bar{H}_\mu$ requires careful consideration. We first note that any composite in $\{X_\mu\}$ with a given power of T_μ and of a given topology can come from terms of different generations of contractions with θ and a global view of the combinatoric factors leads to the exponential structure, $\{e^{\theta}\}$. The details of this algebra have been explained with an example in Appendix D.

Similarly, the RHS can be written as:

$$RHS = \sum_{\mu\nu}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}Y_{\nu\mu}}\}]|\phi_\mu\rangle c_{\mu k} \quad (2.18)$$

yielding the full equation:

$$\sum_{\mu}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}\overline{H}_\mu}\}]|\phi_\mu\rangle c_{\mu k} = \sum_{\mu\nu}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}Y_{\nu\mu}}\}]|\phi_\mu\rangle c_{\mu k} \quad (2.19)$$

In SUMRCC, there is no discrepancy in the number of cluster amplitudes and the number of working equations. Moreover, one may use the invertibility of the coefficient matrix to separate out Eq. 2.19 for each μ.

$$\begin{aligned} \sum_{\mu k}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}\overline{H}_\mu}\}]|\phi_\mu\rangle c_{\mu k}[c^{-1}]_{\lambda k} &= \sum_{\mu\nu k}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}Y_{\nu\mu}}\}]|\phi_\mu\rangle c_{\mu k}[c^{-1}]_{\lambda k} && (2.20)\\ \sum_{\mu}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}\overline{H}_\mu}\}]|\phi_\mu\rangle \delta_{\mu\lambda} &= \sum_{\mu\nu}[\{e^{T_\mu}\}\{\overbracket{e^{\theta}Y_{\nu\mu}}\}]|\phi_\mu\rangle \delta_{\mu\lambda} && (2.21)\\ \{e^{T_\lambda}\}\{\overbracket{e^{\theta}\overline{H}_\lambda}\}|\phi_\lambda\rangle &= \sum_{\nu}[\{e^{T_\lambda}\}\{\overbracket{e^{\theta}Y_{\nu\lambda}}\}]|\phi_\lambda\rangle && (2.22)\end{aligned}$$

Canceling $\{e^{T_\lambda}\}$ from LHS and RHS in Eq. 2.22 and writing λ as μ, the working equation for the amplitudes is simply Eq.2.23:

$$\{\contraction{}{e}{^{\theta}}{\overline{H}}e^{\theta}\overline{H}_{\mu}\}|\phi_{\mu}\rangle - \sum_{\nu}\{\contraction{}{e}{^{\theta}}{Y}e^{\theta}Y_{\nu\mu}\}|\phi_{\mu}\rangle = 0 \tag{2.23}$$

As we have mentioned, our focus is on electron attached/detached and excited states of closed shell ground states, which can be considered as 1-particle (1p)/1-hole (1h) and 1-hole-1-particle (1h-1p) sectors with respect to the closed shell state considered as vacuum respectively. 1h and 1p model spaces are by construction complete (ie. CMS/CAS). The 1h-1p model spaces are said to be "quasi-complete" [5] which is a special case of incomplete model spaces (IMS). In this section, we present the working equations when using a CMS and then discuss the necessary modifications for using an IMS.

For CMS, all the T-operators take us from the model space spanned by the ϕ_μs to the virtual space spanned by the χ_μ^ls and may be called "open" (op) operators. In contrast, $W_{\nu\mu}$ may be called "closed". To get the final working equations, Eq. 2.23 is simply projected by the excited functions to yield Eq. 2.24 which are called projection equations.

$$\langle\chi_{\mu}^{l}|\,\{\contraction{}{e}{^{\theta}}{\overline{H}}e^{\theta}\overline{H}_{\mu}\}|\phi_{\mu}\rangle - \sum_{\nu}\langle\chi_{\mu}^{l}|\,\{\contraction{}{e}{^{\theta}}{Y}e^{\theta}Y_{\nu\mu}\}|\phi_{\mu}\rangle = 0 \tag{2.24}$$

It was found that approximating e^θ to its first term, ie. one, is sufficient, with changes of the order of μH for higher order approximations, and hence, operationally the working equation we use is:

$$\langle\chi_{\mu}^{l}|\{\overline{H}_{\mu}\}|\phi_{\mu}\rangle - \langle\chi_{\mu}^{l}|\sum_{\nu}\{e^{T_{\nu}-T_{\mu}}\contraction{}{e}{^{T_{\nu}}}{W}e^{T_{\nu}}W_{\nu\mu}\}|\phi_{\mu}\rangle \equiv R_{ex,l\mu} = 0 \tag{2.25}$$

For ease of reference we define the composite G_μ at this stage as,

$$G_{\mu} = \{\overline{H}_{\mu}\} - \sum_{\nu}\{e^{T_{\nu}-T_{\mu}}\contraction{}{e}{^{T_{\nu}}}{W}e^{T_{\nu}}W_{\nu\mu}\} \tag{2.26}$$

and write the generic working equation in compact notation as,

$$R_{ex,l\mu} = \langle\chi_{\mu}^{l}|G_{\mu}|\phi_{\mu}\rangle = 0 \tag{2.27}$$

Analogously we get,

$$R_{\lambda\mu} = \langle\phi_{\lambda}|G_{\mu}|\phi_{\mu}\rangle = 0 \tag{2.28}$$

which provides us with the expression for the effective Hamiltonian when the model space is complete.

When the model space is incomplete, $R_{\lambda\mu}$ actually has one portion which is necessary to introduce new cluster operators which are labeled by active lines only for maintaining size extensivity of the energy. The rest of the components of $R_{\lambda\mu}$ are used to define the effective Hamiltonian (see Sec. 2.1.3).

An alternate derivation starting from the Bloch equation [6] also leads to the same final working equation. This route was followed in our publication [7]. Eq. 2.25 is to be used for determining the cluster amplitudes of T_μ.

We note that, the first term, which we henceforth call the "*direct term*", will necessarily truncate at quartic power in all situations. However, the termination of the second, the so-called, "*coupling term*", will depend on the rank of the valence sector under consideration. Since, the working equations are projection equations rather than amplitude-equations (as is commonly used for most CC theories), they involve the occurrence of RDMs which carry the spin information of the targeted molecular states. This feature also complicates the proof of size-extensivity as the RDMs are neither connected nor extensive quantities.

Projecting Eq. 2.19 with the model functions yields the definition for the effective Hamiltonian to be diagonalized to get the targeted state energies without any approximation being required.

$$\sum_{\mu}\langle\phi_\lambda|\,[\{e^{T_\mu}\}\{\overbracket{e^{\theta}\overline{H}}_{\mu}\}]|\phi_\mu\rangle c_{\mu k} = \sum_{\mu\nu}\langle\phi_\lambda|\,[\{e^{T_\mu}\}\{\overbracket{e^{\theta}Y}_{\nu\mu}\}]|\phi_\mu\rangle c_{\mu k} \qquad (2.29)$$

$$\sum_{\mu}\langle\phi_\lambda|\,\{\overline{H}_\mu\}|\phi_\mu\rangle c_{\mu k} = \sum_{\mu\nu}\langle\phi_\lambda|\,\phi_\nu\rangle H_{eff\,\nu\mu}c_{\mu k} \qquad (2.30)$$

$$\sum_{\mu}\langle\phi_\lambda|\,\{\overline{H}_\mu\}|\phi_\mu\rangle c_{\mu k} = \sum_{\mu} H_{eff\,\lambda\mu}c_{\mu k} = E_k c_{\lambda k} \qquad (2.31)$$

$$\Rightarrow H_{eff\,\lambda\mu} = \langle\phi_\lambda|\,\{\overline{H}_\mu\}|\phi_\mu\rangle \qquad (2.32)$$

In going from Eq. 2.29 to Eq. 2.30 we have considered the fact that when acting on a CMS the Ts themselves as well as their products always lead outside the model space. We also note that the same expression for H_{eff} could have been obtained by equating the projection of G_μ, defined in Eq. 2.26, onto the model space to zero (ie.

$R_{cl\lambda\mu} = 0$) as shown below.

$$
\begin{aligned}
R_{cl\lambda\mu} &= 0 \\
\langle\phi_\lambda|\,\{\overline{H}_\mu\}\,|\phi_\mu\rangle &= \sum_\nu \langle\phi_\lambda|\,\{e^{T_\nu - T_\mu}\overline{e^{T_\nu} W}_{\nu\mu}\}\,|\phi_\mu\rangle \\
&= \sum_\nu \langle\phi_\lambda|\,\{W_{\nu\mu}\}\,|\phi_\mu\rangle \\
&= \sum_\nu \langle\phi_\lambda|\,\phi_\nu\rangle H_{eff\nu\mu} \\
&= H_{eff\lambda\mu} \qquad (2.33)
\end{aligned}
$$

We will see in Sec. 2.1.3 how this will turn out to be useful for working in an IMS.

2.1.2 UGA-QFMRCC

The inspiration for the UGA-QFMRCC theory comes from the development of the parent UGA-SUMRCC [7] and the earlier Quasi-Fock theory of Mukhopadhyay and Mukherjee [8]. In the parent UGA-SUMRCC theory, the t-amplitudes required were only those for the target valence sector (say, excited state). Here, our aim is not to obtain the state energy itself but the energy difference with respect to a subduced valence sector (say, ground state). The benefit of a correlated theory for obtaining energy differences directly lies in the exact analytic cancellation of the common correlation energy of the two states, leading to a treatment of the common correlation terms of both states on equal footing even under truncated schemes.

The theory for computing energy differences with respect to the ground state requires an appropriate parametrization of the wave operator where cluster operators inducing correlation of the ground state should also appear explicitly. We use the notation (m,n) to denote an mh-np valence sector and $T^{(m,n)}$ to denote the cluster operators thereof. The theory we will use in this respect first computes the amplitudes for the (0,0) valence sector which generates the cluster operators of the ground state and then−quite unlike the approach of the Fock Space theory−directly computes the amplitudes for the target (m,n) (say,(1,1)) sector. In the FS-MRCC theory, in contrast we would have had to build the target Ω hierarchically, starting from the (0,0) sector of the Fock Space, which is spanned by the HF function, taken as the vacuum. The operators $T^{(1,0)}$ and $T^{(0,1)}$ respectively are constructed in the next stage of solution which provide information of the (1,0) and (0,1) sectors of the Fock Space. Next comes the operators $T^{(1,1)}$ of the target sector, viz. the h-p model space. Our theory bypasses the (1,0) and the (0,1) sectors, and this is the reason why such a theory has been called a Quasi Fock MRCC (QF-MRCC) in the literature [8]. Our intention is to develop a spin-free UGA version of a QF-MRCC, using the same strategy as has been used in our UGA-SUMRCC [7], for the direct computation of such energy differences as ionization potential (IP), electron affinity (EA) and excitation energy (EE). The performance of such a formulation also provides us some insights regarding the physics incorporated in our excited state calculations using UGA-SUMRCC as against that in the description of the ground state using SRCC.

We should mention here that, there exist several closely related theories viz. Valence Universal MRCC (VUMRCC) [9, 10, 11], the so-called double-curly VUMRCC [12, 13] which uses a special combinatoric cluster Ansätz and Similarity Transformed Equation of Motion Coupled Cluster (STEOMCC) [14, 15, 16]. VUMRCC and the double curly VUMRCC utilize a valence universal Ω while all the other methods involve the calculation of ground state amplitudes which are used to transform the Hamiltonian before the computation of the energy differences. UGA-QFMRCC falls in the second category. However, the Ansätz for UGA-QFMRCC is richer in structure and we expect a better performance.

In the present formulation, our first assumption is that the ground state is well described by a single reference theory, viz. the single-reference coupled cluster theory. Therefore, the e^T parametrization of the wave operator, acting on the HF function for the ground state is sufficient. We will treat the excited states as multi-reference in a state universal framework and for the analogous treatment of the common correlation part the cluster amplitudes will include the exact ground state Ts for every model function and the differential correlation will be treated by the S_μ amplitudes. This idea naturally suggests that our choice of Ansätz for UGA-QFMRCC should be of the form:

$$\Omega_\mu = e^T \{e^{S_\mu}\} \tag{2.34}$$

We distinguish carefully between the operators T_μ used in UGA-SUMRCC and S_μ introduced here in the context of UGA-QFMRCC. The T_μs in UGA-SUMRCC represent the actual correlation of the target state contributed by the virtual excitations from ϕ_μ. The S_μs, on the other hand, represent the *differential correlation* and *relaxation* of the state, ie. the difference in the correlation contribution of T_μ of the target state and the subduced state with respect to which the energy difference is required.

We explain below the theory for excitation energy, but the same considerations apply also to any other energy difference of interest. The ground state T-amplitudes are first calculated for the closed shell reference state and so, the first part of our Ansätz is known. The working equations to be derived are thus, for the S_μs of the excited state only. As we have emphasized above, the hierarchical generation of the S_μs going through the various lower valence sectors as in Valence Universal Multireference Coupled Cluster (VUMRCC) [9, 10, 11] is entirely bypassed.

Having solved for T, a dressed Hamiltonian is defined as:

$$\widetilde{H} = e^{-T} H e^{T} \tag{2.35}$$

$\widetilde{H}$ and H_{eff} are now partitioned to separate out the number part, which is the ground state energy, E_{gr}, and the operator parts $\overline{H}$ and $\overline{H}_{eff}$.

$$\widetilde{H} = E_{gr} + \overline{H} \tag{2.36}$$

$$\begin{aligned} H_{eff} = &\quad E_{gr} + \overline{H}_{eff} && (2.37) \\ \overline{H}_{eff\nu\mu} = &\quad \langle \phi_\nu | \overline{W}_{\nu\mu} | \phi_\mu \rangle && (2.38) \end{aligned}$$

$\overline{W}_{\nu\mu}$ may be considered as the closed operator whose matrix element with respect to $\langle \phi_\nu|$ and $|\phi_\mu\rangle$ corresponds to $\overline{H}_{eff\nu\mu}$. Its properties are similar to $W_{\nu\mu}$ discussed in the previous section.

Invoking the Bloch equation for the model function ϕ_μ,

$$\begin{aligned} H\Omega_\mu|\phi_\mu\rangle = &\quad \sum_\nu \Omega_\nu |\phi_\nu\rangle H_{eff\nu\mu} && (2.39) \\ He^{T}\{e^{S_\mu}\}|\phi_\mu\rangle = &\quad \sum_\nu e^{T}\{e^{S_\nu}\}|\phi_\nu\rangle H_{eff\nu\mu} && (2.40) \end{aligned}$$

and operating with e^{-T} from the left, we have

$$\begin{aligned} e^{-T}He^{T}\{e^{S_\mu}\}|\phi_\mu\rangle &= \sum_\nu \{e^{S_\nu}\}|\phi_\nu\rangle H_{eff\nu\mu} && (2.41) \\ \widetilde{H}\{e^{S_\mu}\}|\phi_\mu\rangle &= \sum_\nu \{e^{S_\nu}\}|\phi_\nu\rangle H_{eff\nu\mu} && (2.42) \end{aligned}$$

$$\{e^{S_\mu}\overbracket{\tilde{H}e^{S_\mu}}\}|\phi_\mu\rangle = \sum_\nu \{e^{S_\nu}\}|\phi_\nu\rangle H_{eff\nu\mu} \tag{2.43}$$

Using the definitions in Eqs. 2.36 to 2.38 we can cancel E_{gr} from either side of Eq. 2.43 to give:

$$\begin{aligned} \{e^{S_\mu}\overbracket{\overline{H}e^{S_\mu}}\}|\phi_\mu\rangle &= \sum_\nu \{e^{S_\nu}\overbracket{e^{S_\nu}\overline{W}}_{\nu\mu}\}|\phi_\mu\rangle && (2.44) \\ \{e^{S_\mu}\overbracket{\overline{H}e^{S_\mu}}\}|\phi_\mu\rangle &= \sum_\nu \{e^{S_\mu}e^{-S_\mu}e^{S_\nu}\overbracket{e^{S_\nu}\overline{W}}_{\nu\mu}\}|\phi_\mu\rangle && (2.45) \end{aligned}$$

Eq. 2.45 is satisfied if the following equality is invoked:

$$\{\overbracket{\overline{H}e^{S_\mu}}\}|\phi_\mu\rangle = \sum_\nu \{e^{S_\nu - S_\mu}\overbracket{e^{S_\nu}\overline{W}}_{\nu\mu}\}|\phi_\nu\rangle \tag{2.46}$$

$$\langle\chi_l|\,\{\overline{\overline{H}}\}|\phi_\mu\rangle - \sum_\nu \langle\chi_l|\{e^{S_\nu - S_\mu}\overbracket{e^{S_\nu}\overline{W}}_{\nu\mu}\}|\phi_\nu\rangle = 0 \tag{2.47}$$

Alternatively, we could use Wick's theorem in reverse successively and introduce e^θ as in Eq. 2.19 and then use an approximation for e^θ just like in UGA-SUMRCC (see Sec. 2.1.1).

After having solved for the amplitudes of $\{S_\mu\}$, we obtain the sought after energy differences, ΔE_k and the associated coefficients, $\{c_{\mu k}\}$ from the eigenvalue equation:

$$\sum_\nu \overline{H}_{eff\mu\nu}c_{\nu k} \equiv \sum_\nu \langle\phi_\mu|\overline{W}_{\mu\nu}|\phi_\nu\rangle c_{\nu k} = \Delta E_k c_{\mu k} \tag{2.48}$$

2.1.3 Necessary Modifications for the Use of an Incomplete Model Space (IMS) in the Theories for Excited State Energies and Energy Differences

The essential difficulty of maintaining size extensivity in an incomplete model space is that it is not enough to have an H_{eff} which is connected, since the eigenvalues obtained on eventual diagonalization of even a connected H_{eff} in an IMS would lead to disconnected terms and hence size inextensive energies. The situation is entirely analogous to the diagonalization of a CI matrix in a truncated space where each element of the CI matrix is connected due to the connectedness of H but the diagonalization leads to size inextensive energies. Mukherjee analyzed this issue [17, 18, 19, 20] and concluded that the operator H_{eff} to be diagonalized in the IMS not only should be connected but also should be *closed* in a very special sense. For an IMS, a closed operator should be chosen as one which by construction can never lead to excitation outside the IMS by its action on any ϕ_μ. Given size-extensive T_μs, the simplest choice for getting a size-extensive H_{eff} is *not* to impose the IN: but allow the closed part of $\{e^{T_\mu}\}$ to have the value it should have if Bloch equations are solved without imposing IN [21, 19]. A connected formulation of H_{eff} in an IMS was achieved first in the Fock space MRCC [17, 22, 21, 8], while the corresponding SUMRCC formulation was proposed a few years later [8, 23, 24].

In the most general situation, it is conceivable that an operator labeled by active lines only can lead to a transition from a ϕ_μ to a ϕ_ν but it would not be closed *if there is at least one function* ϕ_λ for which the same operator leads to excitation outside the IMS. They are called *quasi-open* (q-op) operators [21] and since all operators of H_{eff} are labeled by active lines only, one should impose the constraint that the quasi-open components of H_{eff} are zero by construction to ensure that H_{eff} is closed. This is achieved via the inclusion of quasi-open operators in the set $T_\mu \forall \phi_\mu$ and this ensures that the matrix of H_{eff} in the IMS would generally have zero entries connecting the pair (μ, ν) if the corresponding excitation is a quasi-open operator. It is to be emphasized here that once an operator is identified as quasi-open, it should be included in the set T_μ for every ϕ_μ even if its action on that ϕ_μ would lead to another model function ϕ_ν. Of course, one should delete those quasi-open operators in T_μ whose action on ϕ_μ is trivially zero because of Pauli principle. We can thus define two types of T_μs, "open" ($[T_\mu]_{op}$) and "quasi-open" ($[T_\mu]_{q-op}$). The open operators have at least one inactive label, while the quasi-open operators are labeled by active indices only. We should mention that a very comprehensive book-keeping procedure of classifying the various Fock-space operators, where this concept of quasi-open (q-op) and closed is defined by alternative symbols was suggested by Kutzelnigg et al. [18, 25] which provides additional insight into the aspects of connectivity.

For example, in the special case of h-p model spaces, the quasi-open and the closed operators are clearly of different types: any quasi-open operator must involve changes in occupancies of holes and particles and hence, transfer of electrons between active holes and active particles while the closed operators would scatter a h-p function to another h-p function of the h-p model space.These have been termed as 'quasi-complete' by Lindgren [5] For theories involving the h-p IMS having the same symmetry as that of the ground state, a h-p de-excitation operator acting on a ϕ_μ would lead to the Hartree-Fock (HF) function, ϕ_0 which is outside the model space, thus these operators are quasi-open. Also, the h-p excitation operators lead from the model space to 2h-2p virtual functions and these are quasi-open too. Thus in the $\{e^{T_\mu}\}$ there could be a quadratic power ($\{\frac{1}{2}T_\mu^2\}$) where there could be a closed component of the quadratic term arising from the situation where one of the T_μs is a de-excitation and the other is an excitation. Hence, the IN is not satisfied because the powers of quasi-open operators might be closed and we have the relation: $\{e^{T_\mu}\}_{cl} = \{e^{T_{\mu q-op}}\}_{cl}$.

To obtain equations for the quasi-open components of T_μ, we have to project G_μ defined in Eq. 2.26 onto those functions which are reachable by the action of quasi-open operators acting on ϕ_μ. They may, depending on the type of excitation and the ϕ_μ, either belong to the IMS itself or to the 'complementary active space'. The union of the model space and the complementary active space is the complete active space. Defining all such functions reachable by the action of quasi-open operators on ϕ_μ as $\{\bar{\phi}_\mu^\lambda\}$ we would have the corresponding equations for determining the quasi-open operators of T_μ by projecting on to $\langle\bar{\phi}_\mu^\lambda|$. The corresponding residuals for the open and quasi-open T-operators would thus be defined as:

$$R_{l\mu} = \langle \chi_\mu^l | [G_\mu]_{op} | \phi_\mu \rangle \tag{2.49}$$

and,

$$R_{\bar{\lambda}\mu} = \langle \bar{\phi}_{\mu}^{\lambda} | [G_{\mu}]_{q-op} | \phi_{\mu} \rangle. \tag{2.50}$$

Eqs. 2.49 and 2.50 are used to determine $[T_{\mu}]_{op}$ and $[T_{\mu}]_{q-op}$ respectively by the usual updating procedure for the open and the quasi-open amplitudes of T_{μ}. However, they require the knowledge of $W_{\nu\mu}$. This must be obtained from the equation for H_{eff}. *This is where the theories for IMS differ from those for CAS.* In the latter case, H_{eff} is simply the closed part of $\overline{H_{\mu}}$ which can be diagonalized to get the state energies. For IMS-based theories, the H_{eff} is obtained iteratively through the solution of its own equation, just like the T-amplitudes.

We may use sufficiency equations for solving for the amplitudes of T. However, no such freedom is available for the closed component, viz. Eq. 2.28, although a reasonable approximation for e^{θ} which we have taken as one may be deemed acceptable. Since a product of quasi-open operators may be closed, we summarize the rules governing the products of operators in an IMS before defining the H_{eff}:

$$\begin{aligned} cl \times cl &= cl \\ cl \times q-op &= q-op \\ cl \times op &= op \\ q-op \times q-op &= cl \ or \ q-op \\ q-op \times op &= op \\ op \times op &= op \end{aligned} \tag{2.51}$$

Keeping these rules in mind, we may equate $R_{\lambda\mu}$ of Eq. 2.28 to zero to define the H_{eff} in an IMS as in a CMS (Eq. 2.33). For defining the $W_{\nu\mu}$, we now have to make explicit use of the fact that there is a closed component of $\{e^{T_{\mu}}\}$: $\{e^{T_{\mu}}\}_{cl}$. We can have a recursive definition for $W_{\nu\mu}$ from Eq. 2.28. $W_{\lambda\mu}^{i+1}$ is the updated value of the operator $W_{\lambda\mu}$ at the i+1th iteration of the cluster amplitudes. We may initiate the iteration with $W_{\lambda\mu}^{0}$:

$$W_{\lambda\mu}^{0} |\phi_{\mu}\rangle = |\phi_{\lambda}\rangle \langle \phi_{\lambda} | \{\overline{H}_{\mu}\}_{cl} | \phi_{\mu}\rangle \tag{2.52}$$

and continue with,

$$W_{\lambda\mu}^{i+1} |\phi_{\mu}\rangle = \{G_{\mu}\}_{\lambda\mu}^{i} |\phi_{\mu}\rangle + W_{\lambda\mu}^{i} |\phi_{\mu}\rangle \tag{2.53}$$

A special feature of the theory for IMS is that now the coupling term can also contribute to the closed projection. For situations where IN holds good there is no need to update W recursively using Eq. 2.53 but we have instead $W_{\lambda\mu}|\phi_{\mu}\rangle = |\phi_{\lambda}\rangle\langle\phi_{\lambda}|\{\bar{H}_{\mu}\}|\phi_{\mu}\rangle$. A detailed discussion of this procedure is presented in Sec. 5.2.3. Of course, we need to update $\{\bar{H}_{\mu}\}$ after the updating of T_{μ}s. By the same arguments as is adduced in Sec. 2.3 to prove the connectivity of Eq. 2.25, one can infer the connectivities of the Eqs. 2.49 and 2.50 as elaborated later in Sec. 2.3. When IN is abandoned, implicit iteration of $W_{\nu\mu}$ along with the iteration for T-amplitudes leads to convergence of $W_{\nu\mu}$ and hence, equivalently H_{eff}.

Sinha et al. [26] have shown quite some time ago that, in the context of VUMRCC theory for IMS, if only the computation of excitation energy is our target then it is possible, operationally speaking, to ignore the de-excitation quasi-open operators in $\{T_\mu\}$ since the equations for such de-excitation amplitudes are completely decoupled from those of the excitation amplitudes in the sense that in the equations for excitation amplitudes there are no terms containing the de-excitation cluster operators. In effect, this implies that H_{eff} for the h-p IMS does not involve the de-excitation operators at all and we may simply diagonalize H_{eff} in this model space to get excitation energies/excited state energies, depending on the formulation, without the knowledge of the de-excitation cluster amplitudes. Applications of the VUMRCC in this setting have been studied by others as well [27, 28, 29]. However, the analysis of Sinha et al. for the h-p IMS in VUMRCC *is not valid* for the SUMRCC. For UGA-SUMRCC or UGA-QFMRCC, the equations for the excitation and de-excitation operators, E_I^A and E_A^I are coupled and products of E_I^A and E_A^I for the model function, ϕ_I^A, can contribute to the energy via the coupling term in the working equations. Thus, we have proceeded by abandoning IN.

We have also explored the choice of the IMS as comprising of the HF function, ϕ_0 and a set of h-p excited functions ϕ_μ. Such kind of model spaces were first introduced and studied by Kutzelnigg et al. [18, 25] who termed them as 'isolated incomplete model spaces' (IIMS). The IIMS has the interesting property that all quasi-open operators are of excitation type. The de-excitation operators for the h-p model space inducing transitions to the HF ground state function, ϕ_0, in either UGA-SUMRCC or UGA-QFMRCC, do not appear in $\{T_\mu\}$ since this now becomes a closed rather than a quasi-open operator. Thus, for such IIMS, the powers of T_μ which are closed do not then appear at all and the customary IN holds good. We shall study all the three methods, vis. UGA-SUMRCC, UGA-QFMRCC and UGA-IIMS-SUMRCC in the context of core excitation energies.

2.2 The Working Equations in the CCSD Truncation Scheme

We begin with the comment that, in the parent spinorbital-based SUMRCC method using the JM Ansätz in a spinorbital basis, the set of excited functions, $\{\chi_\mu^l\}$, reached by the action of T_μs on the various model functions ϕ_μ, are complete in the sense that for each of the N active model functions, ϕ_μ, if M_μ is the number of virtual functions reached from ϕ_μ, then the total number of cluster amplitudes is $M = \sum_\mu M_\mu$. The corresponding dimension of the Hilbert space spanned by the virtual functions for all the N roots is equal to $M_{virt} = \sum_{l_\mu,k} N_{l_\mu k}$. Since $N_{l_\mu} = M_\mu$, and sum over k is exactly equal to sum over μ, $M_{virt} = M$, and we have no redundancy in the SUMRCC theory. Moreover, in a spinorbital formulation, the virtual determinant, χ^l_μ, reached from a model determinant, ϕ_μ, is uniquely specified by the indices of the occupied and unoccupied spinorbitals in ϕ_μ.

In a spin-free UGA-SUMRCC, one would naturally want to retain the spirit of the spinorbital based SUMRCC but there are two hurdles. Firstly, using a singles and doubles (SD) truncation scheme, not all the virtual functions χ^l_μ generated by single and double orbital substitutions are reachable using one and two body generators of the unitary group accompanying the cluster amplitudes in T_μ in the general situation with arbitrary valence occupancy in the ϕ_μs. Secondly, an overcompleteness can arise within the excitation manifold for one model function, ϕ_μ with more than one T_μ/S_μ leading to the same excited function as the components of T_μ, unlike in the spinorbital-based formulation are not all linearly independent by construction.

We choose to ignore the first hurdle and restrict ourselves to one and two-body operators in T_μ/S_μ to reduce the computational cost and the argument that the use of projection equations involves some three-body composites which partially compensates for this loss of correlation in a somewhat twisted implicit sense.

The second issue poses a serious problem as it is also related to the stability of the solution of the working equations. Since, operators defined in terms of spatial orbitals do not have a one to one correspondence with pairs (χ^l_μ, ϕ_μ), a proper choice of linearly independent operators becomes important. An excited function is characterized by the occupancies of the orbitals and the spin coupling among the singly occupied orbitals. Given the number of open shells (singly occupied orbitals) and the net spin of the state, the number of linearly independent (LIN) functions are known and only as many equations are logically available as there are LIN functions. It is thus theoretically appropriate to choose suitable linearly independent combinations of the various excitation operators of T_μ/S_μ inducing the same orbital occupancy changes in the set $\{\chi^l_\mu\}$.

Li and Paldus have encountered this problem in several UGA-based approaches in the context of SUMRCC [4, 1, 30]. They have attempted two strategies: one in which Gel'fand-Tsetlin (GT) excited states were generated [30, 31] and another in which they exploited the SU2 group adaptation of the generators to form their excitation operators [1]. The generators of Gel'fand states are combined to form the linearly independent operators of an SU2 group in the latter case. These operators will not necessarily follow the one-to-one orthogonality relation of the corresponding Gel'fand adapted excited states of an $U(n_c + n_a + n_v)$ group where n_c denotes the number of inactive core orbitals, n_a denotes the number of active (equivalently, valence) orbitals and n_v denotes the number of inactive virtual orbitals, and they argued that to retain size extensivity, the states must obey this orthogonality relationship. Hence they advocated the use of an orthonormal SU2 adapted manifold of excitation operators.

In our opinion, there are three ways of choosing the cluster operators in such a situation to overcome this hurdle of overcompleteness of the excitation manifold: (a) to use suitable combinations of generators of the unitary group to define the linearly independent combination of excitation operators, (b) to continue to use the simple generators of the unitary group and in case their number exceeds the number of linearly independent excitations, provide extra working equations for the redundant operators by invoking sufficiency conditions and, (c) to use amplitude equations. Approach (b) is entirely conceivable and natural for UGA-SSMRCC, since one is obliged to invoke sufficiency conditions anyway. Such a strategy was indeed adopted by Maitra et.al [32] in their UGA-SSMRCC and a related theory where the inactive double excitations were treated in an internally contracted manner (UGA-ICID-SSMRCC) [33]. In the realm of UGA-SUMRCC such sufficiency conditions do not appear but it is not mandatory to disallow redundancy such as has been employed in the UGA-SSMRCC. The use of redundant cluster operators may lead to simpler working equations whose efficacy needs to be looked into. In our UGA-SUMRCC and UGA-QFMRCC formulation [7, 34] we have explored both strategies (a) and (b) to study their relative performance. In Sec. 2.2.1 we discuss how we can use simple perturbative arguments to choose the LIN combinations of T-operators for approach (a) and in Sec. 2.2.2 we discuss how suitable sufficiency conditions may be chosen for approach (b). The third possibility, (c), is to abandon the projection equations altogether and solve the amplitude equations. The question of linear dependencies does not arise in this case. The equations are then also easily extendible to arbitrary valence sectors. In this sense, this possibility is - theoretically speaking - superior to the second option of using sufficiency conditions. On the flip side, amplitude equations involve less terms than the corresponding projection equations and some compromise in terms of accuracy has to be made. We discuss the details of this approach in Sec. 2.2.3.

2.2.1 Projection Equations: Scheme P

This is the most rigorous and elaborate scheme we will apply where all G blocks up to three body with direct and exchange spectator scatterings are included in the projection equations. The equations for the 1h-1p valence sector may involve three and four body blocks. We have ignored the four body blocks since, they arise from nonlinear coupled cluster terms and are found to have very small contributions. In this scheme the excitation manifold is taken to be linearly independent and appropriate combinations are chosen by the method delineated below.

Use of Non-redundant Excitation Manifold

In the present formalism we have generated the working equations by projecting the set of Bloch equations to the excited state CSFs, χ_μ^l. We want our operators to be LIN although not necessarily orthogonal. We propose to choose our combinations of operators in a practicable manner within the framework of our theory, using a two-pronged approach: a perturbative analysis of our working equations and the knowledge of the number of LIN functions. Whether these operators produce mutually orthogonal virtual functions, is something we do not consider at all. We illustrate our scheme using an example.

We will henceforth denote by labels i, j, ..., etc. the inactive holes, by a, b, ..., etc. the inactive particles, by I, J, ..., etc. the active holes and by A, B, ...,etc. the active particles. Excitations involving an orbital, 'i', and an orbital, 'a', can belong to two classes: (i) not involving a change in occupancy of the active hole (I) or particle (A) orbitals or (ii) involving a change in occupancy of the active hole or particle orbitals. t_i^a, t_{iI}^{Ia} and t_{iA}^{Aa} belong to the first class. It is enough if we explain our strategy using the Ts belonging to this class. For those belonging to the second class, like t_{ij}^{Aa} or t_{IA}^{ab}, etc., an exactly analogous analysis can be used.

To discern which of the excitation operators accompanying the amplitudes, t_i^a, t_{iI}^{Ia} and t_{iA}^{Aa} are linearly independent we first look carefully at the algebraic structures of their working equations: viz. Eqs. 2.54, 2.55 and 2.56:

$$
\begin{aligned}
G_i^a - G_{iI}^{aI}\eta_I^I + G_{iA}^{aA}\gamma_A^A - \frac{1}{2}G_{iI}^{Ia}\eta_I^I - \frac{1}{2}G_{iA}^{Aa}\gamma_A^A + G_{iIA}^{aIA}\Gamma_{IA}^{IA} - \frac{1}{2}G_{iAI}^{AaI}\Gamma_{IA}^{IA}& \\
-\frac{1}{2}G_{iIA}^{IaA}\Gamma_{IA}^{IA} + G_{iIA}^{aAI}\Gamma_{IA}^{AI} - \frac{1}{2}G_{iIA}^{AaI}\Gamma_{IA}^{AI} - \frac{1}{2}G_{iAI}^{IaA}\Gamma_{IA}^{AI} = 0& \qquad (2.54)\\
G_i^a\eta_I^I - G_{iI}^{aI}\eta_I^I - G_{iA}^{aA}\Gamma_{IA}^{IA} + 2G_{iI}^{Ia}\eta_I^I - G_{iA}^{Aa}\Gamma_{AI}^{IA} + G_{iIA}^{aIA}\Gamma_{IA}^{IA} + G_{iIA}^{AIa}\Gamma_{IA}^{AI}& \\
-2G_{iIA}^{IaA}\Gamma_{IA}^{IA} + G_{iIA}^{aAI}\Gamma_{IA}^{AI} - 2G_{IiA}^{aAI}\Gamma_{IA}^{AI} + G_{iAI}^{IaA}\Gamma_{IA}^{IA} = 0& \qquad (2.55)\\
-G_i^a\gamma_A^A - G_{iI}^{aI}\Gamma_{IA}^{IA} - G_{iA}^{aA}\gamma_A^A - G_{iI}^{Ia}\Gamma_{AI}^{IA} + 2G_{iA}^{Aa}\gamma_A^A - G_{iIA}^{aIA}\Gamma_{IA}^{IA} + 2G_{iIA}^{AIa}\Gamma_{IA}^{IA}& \\
-G_{iIA}^{IaA}\Gamma_{IA}^{AI} - G_{iIA}^{aAI}\Gamma_{IA}^{AI} + 2G_{IiA}^{aAI}\Gamma_{IA}^{AI} + G_{iAI}^{IaA}\Gamma_{IA}^{IA} = 0& \qquad (2.56)
\end{aligned}
$$

The values of the RDMs featuring in this equation have the following values for the h-p case.

$$
\begin{aligned}
\gamma_A^A =& \quad \langle\phi_\mu|\{E_A^A\}|\phi_\mu\rangle = 1 \\
\eta_I^I =& \quad 2 - \langle\phi_\mu|\{E_I^I\}|\phi_\mu\rangle = 2 - \gamma_I^I = 1 \qquad (2.57)\\
\Gamma_{IA}^{IA} =& \quad \langle\phi_\mu|\{E_{IA}^{IA}\}|\phi_\mu\rangle = -1 \\
\Gamma_{IA}^{AI} =& \quad \langle\phi_\mu|\{E_{IA}^{AI}\}|\phi_\mu\rangle = 1 + (-1)^S \qquad (2.58)
\end{aligned}
$$

where S is the spin of the CSF, ϕ_μ (ie. S=0 for singlet and S=1 for triplet). The symbols γ and η refer to particle and hole densities respectively. To obtain the LIN combinations of operators it is sufficient to consider up to two-body G-blocks.

For the singlet excited states, using the values of the RDMs as in Eq. 2.57 , we arrive at the following equations:

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} + \frac{1}{2}G_{iI}^{Ia} - \frac{1}{2}G_{iA}^{Aa} = 0 \tag{2.59}$$

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} + 2G_{iI}^{Ia} - 2G_{iA}^{Aa} = 0 \tag{2.60}$$

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} + 2G_{iI}^{Ia} - 2G_{iA}^{Aa} = 0 \tag{2.61}$$

Similarly, the equations for triplet states are:

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} + \frac{1}{2}G_{iI}^{Ia} - \frac{1}{2}G_{iA}^{Aa} = 0 \tag{2.62}$$

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} + 2G_{iI}^{Ia} = 0 \tag{2.63}$$

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} - 2G_{iA}^{Aa} = 0 \tag{2.64}$$

We note here that Eqs. 2.60 and 2.61 are identical. Thus, t_{iI}^{Ia} and t_{iA}^{Aa} are linearly dependent operators. After a slight mathematical manipulation, the set of equations, Eqs. 2.59-2.61, can be equivalently written as:

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} = 0 \tag{2.65}$$

$$G_{iI}^{Ia} - G_{iA}^{Aa} = 0 \tag{2.66}$$

The first order perturbative estimate of the cluster amplitude t_i^a from Eq. 2.65 is given by

$${}^1t_i^{a(1)} \approx \frac{(f_i^a - V_{iI}^{aI} + V_{iA}^{aA})\{E_i^a\}}{f_i^i - V_{iI}^{iI} + V_{iA}^{iA} - f_a^a + V_{aI}^{aI} - V_{aA}^{aA}} = {}^1t_i^{a(1)}\{E_i^a\}. \tag{2.67}$$

Similarly, Eq. 2.66 indicates that

$${}^2t_i^{a(1)} \approx \frac{(V_{iI}^{Ia} - V_{iA}^{Aa})}{f_i^i - V_{iI}^{iI} + V_{iA}^{iA} - f_a^a + V_{aI}^{aI} - V_{aA}^{aA}} \tag{2.68}$$

The quantities f_p^p, (p = i or a), are orbital energies and V_{rs}^{pq} are the two-body matrix elements of the Coulomb repulsion operator. Thus, the corresponding operators, $\{E_{iI}^{Ia}\}$ and $\{E_{iA}^{Aa}\}$ should be treated on the same footing in a combination as guided by the first order estimate. We should therefore introduce ${}^2T_i^a \equiv^2 t_i^a[\{E_{iI}^{Ia}\} - \{E_{iA}^{Aa}\}]$ with a common amplitude ${}^2t_i^a$ as the unknown and use Eq. 2.66 for its determination.

Thus the first class of operators contains:${}^1t_i^a\{E_i^a\}$ and ${}^2T_i^a =^2 t_i^a[\{E_{iA}^{Aa}\} - \{E_{iI}^{Ia}\}]$. Similarly the second class of operators contains: ${}^1\tilde{T}_i^a =^1 \tilde{t}_i^a[\{E_{iI}^{aA}\} - 0.5\{E_{iI}^{Aa}\}]$ and ${}^2\tilde{T}_i^a =^2 \tilde{t}_i^a[\{E_{iA}^{aI}\} - 0.5\{E_{iA}^{Ia}\}]$. The triplet equations, on the other hand, do not indicate

Table 2.1: **Choices of Ts for Singlet 1h-1p States**

	UGA-SUMRCC	OSCC (Paldus and Li) [4]
T_i^I	$t_i^I\{E_i^I\}$	$t_i^I\{E_i^I\}$
T_i^A	$t_i^A\{E_i^A\}$	$t_i^A\{E_i^A\}$
T_I^a	$t_I^a\{E_I^a\}$	$t_I^a\{E_I^a\}$
T_A^a	$t_A^a\{E_A^a\}$	$t_A^a\{E_A^a\}$
${}^1T_i^a$	${}^1t_i^a\{E_i^a\}$	$\frac{1}{\sqrt{2}}{}^1t_i^a\{E_i^a\}$
${}^2T_i^a$	${}^2t_i^a[\{E_{iA}^{Aa}\}-\{E_{iI}^{Ia}\}]$	$\frac{1}{\sqrt{2}}{}^2t_i^a[\{E_{iI}^{Ia}\}-\{E_{iA}^{Aa}\}-\{E_i^a\}]$
$T_{ij}^{\bullet\bullet}$	$t_{ij}^{\bullet\bullet}[\{E_{ij}^{IA}\}+\{E_{ij}^{AI}\}]$	$\frac{1}{\sqrt{2}}t_{ij}^{\bullet\bullet}[\{E_{ij}^{IA}\}+\{E_{ij}^{AI}\}]$
$T_{\bullet\bullet}^{ab}$	$t_{\bullet\bullet}^{ab}[\{E_{IA}^{ab}\}+\{E_{AI}^{ab}\}]$	$\frac{1}{\sqrt{2}}t_{\bullet\bullet}^{ab}[\{E_{IA}^{ab}\}+\{E_{AI}^{ab}\}]$
$\tilde{T}_i^a$	${}^1\tilde{t}_i^a[\{E_{iI}^{aA}\}-0.5\{E_{iI}^{Aa}\}]$	${}^1\tilde{t}_i^a[\{E_{iI}^{aA}\}+\{E_{iI}^{Aa}\}]$
	${}^2\tilde{t}_i^a[\{E_{iA}^{aI}\}-0.5\{E_{iA}^{Ia}\}]$	${}^2\tilde{t}_i^a[\{E_{iA}^{aI}\}+\{E_{iA}^{Ia}\}]$
T_{ii}^{aa}	$t_{ii}^{aa}\{E_{ii}^{aa}\}$	$\frac{1}{2}t_{ii}^{aa}\{E_{ii}^{aa}\}$
T_{ii}^{ab}	$t_{ii}^{ab}\{E_{ii}^{ab}\}$	$\frac{1}{\sqrt{2}}t_{ii}^{ab}\{E_{ii}^{ab}\}$
T_{ij}^{aa}	$t_{ij}^{aa}\{E_{ij}^{aa}\}$	$\frac{1}{\sqrt{2}}t_{ij}^{aa}\{E_{ij}^{aa}\}$
T_{ij}^{ab}	$t_{ij}^{ab}\{E_{ij}^{ab}\}$	$\frac{1}{2}{}^1t_{ij}^{ab}[\{E_{ij}^{ab}\}+\{E_{ij}^{ba}\}]$
	$t_{ij}^{ba}\{E_{ij}^{ba}\}$	$\frac{1}{2\sqrt{3}}{}^2t_{ij}^{ab}[\{E_{ij}^{ab}\}-\{E_{ij}^{ba}\}]$

any linear dependence and hence, all three operators, t_i^a, t_{iI}^{Ia} and t_{iA}^{Aa} can be used.

A comparative list of the operators used by us against those chosen by Li and Paldus [4] are provided in Table 2.1 and Table 2.2 wherein the operators chosen by Li and Paldus [4] have been converted to normal order with respect to the HF function for an easy comparison with our manifold of operators.

The perturbative analysis is workable in a straightforward manner only up to two body operators. In the case of a two active electron situation, we know that the excited functions must be either symmetric (triplet) or anti-symmetric (singlet) depending on whether the model function is triplet or singlet respectively. This consideration allows us to construct combinations of operators. Beyond two body operators, for more than two active electrons, taking explicit combination of operators becomes rather cumbersome and difficult in any scheme but doable in principle via the combination of generators of the unitary group adapted to SU2, for instance, with or without orthogonality.

2.2.2 Deliberate Use of Sufficiency Conditions: Scheme S

In the previous subsection, we have seen that suitable combinations of operators need to be chosen to ensure a linearly independent excitation manifold. This would become increasingly complicated as we proceed to higher valence sectors. There is a possibility that inflating the number of equations by invoking sufficiency conditions

Table 2.2: **Choices of Ts for Triplet 1h-1p States**

	UGA-SUMRCC	OSCC (Paldus and Li) [4]
T_i^I	$t_i^I\{E_i^I\}$	$t_i^I\{E_i^I\}$
T_i^A	$t_i^A\{E_i^A\}$	$t_i^A\{E_i^A\}$
T_I^a	$t_I^a\{E_I^a\}$	$t_I^a\{E_I^a\}$
T_A^a	$t_A^a\{E_A^a\}$	$t_A^a\{E_A^a\}$
T_i^a	$t_i^a\{E_i^a\}$	$\frac{1}{\sqrt{2}}\,{}^{1}t_i^a\{E_i^a\}$
T_{iI}^{Ia}	$t_{iI}^{Ia}\{E_{iI}^{Ia}\}$	$\frac{1}{\sqrt{2}}\,{}^{2}t_i^a[\{E_{iI}^{Ia}\}-\{E_{iA}^{Aa}\}-\{E_i^a\}]$
T_{iA}^{Aa}	$t_{iA}^{Aa}\{E_{iA}^{Aa}\}$	$\frac{1}{2}\,{}^{3}t_i^a[\{E_{iI}^{Ia}\}+\{E_{iA}^{Aa}\}]$
$T_{ij}^{\bullet\bullet}$	$t_{ij}^{\bullet\bullet}[\{E_{ij}^{IA}\}-\{E_{ij}^{AI}\}]$	$\frac{1}{2}t_{ij}^{\bullet\bullet}[\{E_{ij}^{IA}\}-\{E_{ij}^{AI}\}]$
$T_{\bullet\bullet}^{ab}$	$t_{\bullet\bullet}^{ab}[\{E_{IA}^{ab}\}-\{E_{AI}^{ab}\}]$	$\frac{1}{2}t_{\bullet\bullet}^{ab}[\{E_{IA}^{ab}\}-\{E_{AI}^{ab}\}]$
T_{iI}^{Aa}	$t_{iI}^{Aa}\{E_{iI}^{Aa}\}$	$t_{iI}^{Aa}\{E_{iI}^{Aa}\}$
T_{ij}^{aI}	$t_{ij}^{aI}\{E_{ij}^{aI}\}$	$\frac{1}{\sqrt{2(1+\delta_{ij})}}\,{}^{1}t_{ij}^{aI}[\{E_{ij}^{aI}\}+\{E_{ji}^{aI}\}]$
T_{ji}^{aI}	$t_{ji}^{aI}\{E_{ji}^{aI}\}$	$\frac{1}{\sqrt{6}}\,{}^{2}t_{ij}^{aI}[\{E_{ji}^{aI}\}-\{E_{ij}^{aI}\}]$
T_{ij}^{aA}	$t_{ij}^{aA}\{E_{ij}^{aA}\}$	$\frac{1}{\sqrt{2(1+\delta_{ij})}}\,{}^{1}t_{ij}^{aA}[\{E_{ij}^{aA}\}+\{E_{ji}^{aA}\}]$
T_{ji}^{aA}	$t_{ji}^{aA}\{E_{ji}^{aA}\}$	$\frac{1}{\sqrt{6}}\,{}^{2}t_{ij}^{aA}[\{E_{ji}^{aA}\}-\{E_{ij}^{aA}\}]$
T_{iI}^{ab}	$t_{iI}^{ab}\{E_{iI}^{ab}\}$	$\frac{1}{\sqrt{2(1+\delta_{ab})}}\,{}^{1}t_{iI}^{ab}[\{E_{iI}^{ab}\}+\{E_{iI}^{ba}\}]$
T_{iI}^{ba}	$t_{iI}^{ba}\{E_{iI}^{ba}\}$	$\frac{1}{\sqrt{6}}\,{}^{2}t_{iI}^{ba}[\{E_{iI}^{ba}\}-\{E_{iI}^{ba}\}]$
T_{iA}^{ab}	$t_{iA}^{ab}\{E_{iA}^{ab}\}$	$\frac{1}{\sqrt{2(1+\delta_{ab})}}\,{}^{1}t_{iA}^{ab}[\{E_{iA}^{ab}\}+\{E_{iA}^{ba}\}]$
T_{iA}^{ba}	$t_{iA}^{ba}\{E_{iA}^{ba}\}$	$\frac{1}{\sqrt{6}}\,{}^{2}t_{iA}^{ba}[\{E_{iA}^{ba}\}-\{E_{iA}^{ba}\}]$
T_{ii}^{aa}	$t_{ii}^{aa}\{E_{ii}^{aa}\}$	$\frac{1}{2}t_{ii}^{aa}\{E_{ii}^{aa}\}$
T_{ii}^{ab}	$t_{ii}^{ab}\{E_{ii}^{ab}\}$	$\frac{1}{\sqrt{2}}t_{ii}^{ab}\{E_{ii}^{ab}\}$
T_{ij}^{aa}	$t_{ij}^{aa}\{E_{ij}^{aa}\}$	$\frac{1}{\sqrt{2}}t_{ij}^{aa}\{E_{ij}^{aa}\}$
T_{ij}^{ab}	$t_{ij}^{ab}\{E_{ij}^{ab}\}$	$\frac{1}{2}\,{}^{1}t_{ij}^{ab}[\{E_{ij}^{ab}\}+\{E_{ij}^{ba}\}]$
T_{ij}^{ba}	$t_{ij}^{ba}\{E_{ij}^{ba}\}$	$\frac{1}{2\sqrt{3}}\,{}^{2}t_{ij}^{ab}[\{E_{ij}^{ab}\}-\{E_{ij}^{ba}\}]$

would allow us to use all possible generators of the unitary group (E) without having to bother about what combination to use. We explore this possibility for a 1h-1p sector using both UGA-SUMRCC and UGA-QFMRCC. The true benefit of this scheme is, however, expected to be in the extension of these theories to higher valence sectors and higher body T operators. In the context of the example mentioned in Sec. 2.2.1, this would mean using the following set of equations.

$$G_i^a - G_{iI}^{aI} + G_{iA}^{aA} - G_{iIA}^{aIA} + 2G_{iIA}^{aAI} - G_{iAI}^{IaA} = 0 \tag{2.69}$$

$$G_{iI}^{Ia} + G_{iIA}^{IaA} - G_{IiA}^{aAI} = 0 \tag{2.70}$$

$$G_{iA}^{Aa} - G_{iIA}^{AIa} + G_{IiA}^{aAI} = 0 \tag{2.71}$$

Similarly, the equations for the other dependent operators may be separated out. However, this separation is sometimes ambiguous leading to the possibility of arbitrary equations. The excitation manifold here is over-complete with the same function generated more than once. Unlike the orthogonal space of Gel'fand adapted excited functions, our manifold in the Scheme P of the UGA-SUMRCC is chosen to be linearly independent but is not orthogonal. On invoking sufficiency, the dependent operators can be treated as independent. This might destroy the relative contribution of these amplitudes rendering the equations unstable, inaccurate or both. The performance of this approximation with artificial inflation of unknowns and equations has thus to be carefully assessed to test its efficacy. The results are presented in Sec. 2.4. A further approximation leads to Scheme S′ wherein only the G-blocks which are proportional feature. We must indicate here that G_{iIA}^{aAI} is not proportional to G_i^a although the operator $\{E_{iIA}^{aAI}\}$ is factorizable into $\{E_i^a\}\{E_{IA}^{AI}\}$ as $\{E_{IA}^{AI}\}$ is not a number operator for the CSF, ϕ_μ.

2.2.3 The Amplitude Equations: Scheme A

While a set of sufficiency equations may be deduced from the parent projection equations, an equally feasible approach is to use operator equations or, as they are commonly called, amplitude equations. This approach does not require any consideration of linear dependence as the equations do not correspond to the action of operators on any function space. As in Scheme S′, only the G-blocks which are proportional to each other appear in the same equation. For example, for a 1h-1p,(I,A), model function G_{ijI}^{aIb} occurs in the equation for T_{ij}^{ab} which involves an exchange spectator scattering in $j \rightarrow b$. An exchange spectator scattering can result in a spin flip along with a double excitation. The operators of these G-blocks excite to functions not spanned by the manifold of our T-operators. Moreover, those G blocks which are not proportional to the lower body one or two-body operators appear at higher orders of perturbation. These are not present in the amplitude equations of Scheme A, thereby yielding simpler equations and facilitating the reduction of computational cost as well.

2.2.4 Equivalence of Projection and Amplitude Equations

For our UGA-SUMRCC, the presence of the RDMs in the working equations means that the set of working equations for Scheme P have the structure:

$$R^l_\mu = \sum_{l'} \langle\phi_\mu| E^{l\,\dagger}_\mu \bar{E}^{l'}_\mu |\phi_\mu\rangle\, g = Dg = 0 \tag{2.72}$$

where ‘g’ is the amplitude of the G-block, G, and D is the overlap matrix between the cluster operators and the operators associated with the G-blocks. It is important to note that the excited functions denoted by the superscripts, l and l’, have exactly the same orbital occupancies but may differ in the spin-coupling schemes. By the property of orthogonality of Gel’fand states, such overlap elements will be zero. It is also important to note that for the choice of G-blocks in Scheme P, D is a rectangular matrix as three and higher body G-blocks which are not proportional to any cluster operator in our CCSD truncation scheme occur in the projection equations. D is thus not invertible. However, if we discard such G-blocks and only allow projections of the LIN cluster operators, D will turn out to be a square, non-singular and hence, invertible matrix leading to:

$$g^l_\mu = 0 \;\forall\; l. \tag{2.73}$$

This is, of course, the structure of the amplitude equations of Scheme A.

Hence, we can summarize that Scheme P is a rigorous scheme of projection equations with the highest inclusion of physics while Scheme A, a perfectly valid approach involving amplitude equations may be shown to be equivalent to a simplified projection scheme with comparatively less physics. The sufficiency equations of Scheme S and their simplified versions in Scheme S$'$ are somewhat arbitrary and may show erratic behavior. Scheme S$'$ turns out to be very close to using amplitude equations although the theoretical premise of operator equations vis a vis projection equations is considerably different. In fact, the explicit equations for 1h, 1p and 1h-1p triplet states are exactly the same for Schemes S$'$ and A.

2.3 Size Extensivity of the Parent UGA-SUMRCC and Evaluation of Size Intensive Energy Differences in UGA-QFMRCC

In this section we discuss the aspects of size-extensivity of UGA-SUMRCC and further elaborate on how the extensivity of the cluster amplitudes may be inferred in spite of the occurrence of inextensive quantities, ie. the RDMs, in the working equations. To aid in the development of our arguments, we concisely rewrite Eq. 2.25 as:

$$\sum_{n} \langle \chi_{\mu}^{l} | G_{\mu}^{l(n)} | \phi_{\mu} \rangle = 0 \tag{2.74}$$

where,

$$G_{\mu}^{l(n)} = \{\overline{H}_{\mu}\}^{(n)} - \sum_{\nu} \{ e^{T_\nu - T_\mu} \contraction{}{e^{T_\nu}}{}{W} e^{T_\nu} W_{\nu\mu} \}^{(n)}. \tag{2.75}$$

'n' denotes the rank of the operator. There are two levels of connectivity to be analyzed. First, we must demonstrate that the $G_{\mu}^{l(n)}$ blocks themselves are connected composites. Next, we must be able to show that the different components of the working equations obtained on projection by $\langle \chi_{\mu}^{l} |$ do not lead to disconnected pieces in the H_{eff} which would lead to the energies being size-inextensive. Since RDMs are not, in general, connected quantities, we must conclusively show that all of the terms in the matrix element $\langle \chi_{\mu}^{l} | G_{\mu}^{l(n)} | \phi_{\mu} \rangle$, with the potential of being disconnected, either necessarily have common labels with the G-blocks or cancel on algebraic manipulation. In essence one needs to show that the terms contributing to each projection equation are connected entities. Subsequently, one must establish that at the asymptotic separation of the molecule into fragments, say, A and B, T_{μ}s labeled by orbitals on both A and B are necessarily zero, in order to conclusively prove the additive separability of the energy.

It is possible to demonstrate the connectedness of the working equations by a cumulant decomposition of the RDMs featuring in our working equations followed by a substitution of the equations for lower rank cluster operators in the equations for higher rank operators in order to remove disconnected entities but this does not help us in easily demonstrating the extensivity of the theory. The demonstration of connectedness of the equations is presented in Appendix E. In this thesis, we restrict ourselves to the 1h, 1p and 1h-1p spaces and present a proof of extensivity for these specific situations only.

2.3.1 Connectivity of the G_{μ} Blocks

To start with, we assume that the cluster amplitudes are connected and analyze the connectivity of the G-blocks. The G-blocks are composed of two types of terms, the so-called "*direct term*" and the "*coupling term*". The composite quantity, $\bar{H}_{\mu}$, is an explicitly connected quantity if the T_{μ}s are connected. Hence, the direct terms are connected. For the coupling term, we have to analyze several different aspects of the connectivity:

1) Connectivity of $\overbracket{e^{T_\nu}W}_{\nu\mu}$: $W_{\nu\mu}$ consists of those closed components of $\bar{H}_\mu$ which excites ϕ_μ to ϕ_ν and being a part of $\bar{H}_\mu$ is explicitly connected. For connected T_ν s, $\overbracket{e^{T_\nu}W}_{\nu\mu}$ is explicitly connected. In what follows we will henceforth denote $\overbracket{e^{T_\nu}W}_{\nu\mu}$ as $\zeta_{\nu\mu}$

2) Connectivity of $\{e^{T_\nu - T_\mu}\zeta_{\nu\mu}\}$: We consider two possible cases here; the case where ϕ_ν and ϕ_μ differ by at least one orbital (Case 2a) and the case where ϕ_μ and ϕ_ν have the same orbital occupancy and either $\phi_\mu = \phi_\nu$ or they differ in the spin coupling scheme of the active orbitals (Case 2b).

For Case 2a, the quantity $\zeta_{\nu\mu}$ is explicitly dependent on all the active orbitals by which ϕ_μ and ϕ_ν differ since $\zeta_{\nu\mu}$ contains $W_{\nu\mu}$. Since all the CSFs in the model spaces are treated on the same footing, the functional dependence of every cluster amplitude on the active orbital labels remains the same. Hence, the difference of the amplitudes $t_\mu - t_\nu$ inducing the same excitation depends implicitly on one or more of the active orbitals by which ϕ_μ and ϕ_ν differ. Hence the composite $\{e^{T_\nu - T_\mu}\zeta_{\nu\mu}\}$ have at least one common active orbital label shared by the two factors and hence, the composite is connected. We also note here that our analysis subsumes the case where some components of T_ν are zero in the coupling term in Eq. 2.25 because of the occupancy restrictions of some active orbitals. Clearly, the corresponding T_μ involving the same label of active orbitals in creation and destruction must involve those orbitals by which ϕ_μ and ϕ_ν differ.

For Case 2b, if ϕ_μ and ϕ_ν are the same, the composite in the coupling term reduces simply to $\zeta_{\nu\mu}$ which is obviously connected. If ϕ_μ and ϕ_ν have the same orbital occupancy but differ in their spin coupling schemes, then the quantity $\zeta_{\nu\mu}$ would depend on one or more of the same orbitals involved in the different spin couplings for ϕ_μ and ϕ_ν. In such a situation, the difference $t_\mu - t_\nu$ will have implicit dependence on all active orbitals involved in the segments in which the spin couplings of ϕ_μ and ϕ_ν are different, and hence the product $\{e^{T_\nu - T_\mu}\zeta_{\nu\mu}\}$ is a connected term.

2.3.2 Extensivity of the Cluster Amplitudes

In order to establish the size-extensivity of the UGA-SUMRCC theory, the requirement is that energy of the system, AB, with sub-systems A and B at infinite separation, should not have any contribution from the T_{AB}s which are T_μs bearing orbital labels belonging to both sub-systems A and B. Usually (for example, for spinorbital-based SUMRCC or SSMRCC), the more stringent condition of $T_{AB} = 0$ is satisfied.

If one considers the basic projection equations, for example, as in Eqs. 2.59-2.61, it would appear that disconnected components are present, viz. G_i^a and G_{iA}^{aA} in Eq. 2.60 contributing to R_{iI}^{Ia} and G_i^a and G_{iI}^{Ia} in Eq. 2.61 contributing to R_{iA}^{Aa}. However, once the coupled equations are decoupled by simple algebraic manipulation as shown in Sec. 2.2.1, not only can we identify the LIN combinations of operators but also understand the extensivity of the cluster operators. The decoupled equations as shown in Eq. 2.65 and Eq. 2.66, for instance, indicate that no disconnected terms involving lower rank G-blocks occur at all. Thus, at the asymptotic limit of infinite separation of fragments (say, A and B), the T_{AB}s at the initial perturbative level are zero owing to the additive separability of the Hamiltonian, $H = H_A + H_B; H_{AB} = 0$. Stemming from the connectivity of the G-blocks, as established in Sec. 2.3.1, and the extensivity of the Hamiltonian, a G-block of the AB type cannot be constructed from pure T_As and/or T_Bs. Thus, no R_{AB} is ever generated and the T_{AB}s remain zero throughout the iterative procedure. Specifically for the example we are discussing, if i,a and I are on fragment A and orbital A is on fragment B, the t-amplitude associated with the operator $E^{Ia}_{iI} - E^{Aa}_{iA}$ is still entirely on fragment A as Hamiltonian contractions with E^{Aa}_{iA} will be zero.

A similar analysis can establish the size-extensivity of the state energies, $E_{gr}+\Delta E$, ΔE being computed using the UGA-QFMRCC theory. Since, E_{gr} is the CCSD energy for the closed shell ground state and is thus extensive, the intensivity of ΔE is proved.

2.4 Molecular Applications

Our goal in this section is twofold: to study the accuracy of the UGA-SUMRCC and UGA-QFMRCC theories proposed by us against other comparable theories for ionized and excited state energies and to explore the inherent performance of the theories in view of the flexibility afforded to us by the choice of projection versus sufficiency equations or projection versus amplitude equations and the set of G-blocks to be considered.

Our theories are expected to be more accurate than EOM-CCSD as a result of the greater richness of physics of our wave operator Ω on two counts. First, the R_k operators in EOM-CC (as in Eq. F.8) truncate at the linear term as in the linear response theories resulting in an incomplete description of the Thouless-like orbital relaxation. Our method allows a much higher degree of clustering. Our results corroborate this expectation. The SU-COSCC Ansätz of Datta and Mukherjee [35] takes this clustering even further by allowing T-T contraction with suitable combinatoric factors making it a possible theory for benchmarking for us. We find that the gain in terms of simplicity of formulation and implementation of the UGA-MRCC theories outweighs the loss in accuracy with respect to the COSCC Ansätz. Secondly, EOM-CC cluster amplitudes are defined with respect to the ground state while our ts being μ dependent along with suitable use of spectator blocks leads to properly corrected excited state amplitudes. A complete theoretical comparison of our theories and the various EOM-CC/LRT and COS-CC methods is presented in Sec. 3.2 especially in the context of orbital relaxation.

In this section, we undertake several exploratory studies of inherent accuracy of the UGA-SUMRCC and UGA-QFMRCC theories, comparisons between the two theories as well as the relative efficacy and consistency of the various schemes proposed by us in Sec. 2.2. We test the performance of our new Ansätze for three valence sectors: electron detached states, electron attached states and excited states by benchmarking our results against FCI wherever possible. Scheme P is the most elaborate scheme proposed by us and the performance of the other three approaches, viz. Schemes S, S′ and A, may be studied against it.

As mentioned before, for the 1h and 1p valence sectors, to which the electron attached and detached states of closed shell molecules and neutral radicals studied by us belong, Schemes P and S are exactly equivalent as are Schemes A and S′. This stems from the absence of linear dependencies among the cluster operators. Thus, we use these molecular states for comparing the performance of Schemes P and A. Where Scheme P perform significantly worse than Scheme A, we may conclude that the molecule's excited state has significant contribution from these functions and we anticipate that a triples correction involving active orbitals (ie. a CCSDt scheme) will greatly enhance the accuracy of the description. However, we have not pursued this aspect in this thesis. For the 1h-1p sector, linear dependence of cluster operators exists unless proper combinations are taken. Thus, we choose to study the performance of Scheme S vs Scheme P in this valence sector. This aspect is further analyzed by a study on the lowest $^3\Sigma$ state of LiH in Sec. 2.4.5. For larger computations we have indicated the theories and schemes adopted at the appropriate places.

For pilot applications, H_2O, HF^+, $F^{\cdot}$, $CH_3^{\cdot}$, $OH^{\cdot}$ and $NH_2^{\cdot}$ have been chosen as electron detached states and H_2O^- and $CH^{\cdot}$ as electron attached states of the closed shell (0,0) sector. We have chosen the excited states of H_2O, HF, CH_2, BH and CH^+ for comparisons of projection equations vs sufficiency equations in small bases. The tables indicate that the performance of UGA-QFMRCC and UGA-SUMRCC are better than EOMCC and the performance of UGA-QFMRCC and UGA-SUMRCC are comparable to the reference values such as those from FCI and COS-CC results, where available. Subsequently, we present excitation energies in comparison with experimental results for H_2O and C_2H_2. All unreferenced results have been computed by us using GAMESS US- 2007 or 2010 [36]. Results of EOM-CCSD for triplet states have been obtained using DALTON 2.0 [37]. The geometries and basis sets employed for our studies are mentioned as footnotes to the corresponding tables. In all cases we have used orbitals optimized for the vacuum state, specifically the HF function. We could have instead used the optimized orbitals of the corresponding target states provided they are the lowest of their symmetry or some sort of average orbitals. However, the current choice of orbitals allows us to compute several ionized state energies very easily using a common set of orbitals and also provides us an opportunity to demonstrate the strength of our theories to incorporate orbital relaxation effects in an adequate manner.

Our comparison against FCI shows that the full scheme performs pretty well in all cases. Keeping in mind that, being solutions of non-variational equations, the errors may be both positive and negative we see that the full scheme gives results mostly above FCI. The sufficiency variant, S, performs somewhat erratically in the sense it may overshoot or undershoot the FCI values. Though this behavior is not observed in Scheme P, when the comparison is done along different states of a particular molecule, the variants using sufficiency are lacking in this quality. The absolute percentage difference values, on the other hand, shown in Fig. 2.1 clearly show that it is not very large in comparison with FCI values. Schemes A and S$'$, wherein certain three-body blocks have been excluded consistently show a poorer performance indicating that the excluded blocks often play a significant role in the description of excited states.

The bar chart in Fig. 2.1 represents the performance of Scheme S vis a vis Scheme P for different molecules. The results are largely consistent with a few outliers being the $^1A_2$ and $^1B_2$ states of water in cc-pVDZ basis which are of opposite trend from the rest of the bases (please refer to Table 2.13) though, in an absolute sense, these differences are not very large. The reason may lie in some sort of inadequate description of these states in cc-pVDZ basis. We have also seen that the difference values may be positive or negative which indicates that both ordinary mean and absolute mean would be necessary to get a feeling of the performance of sufficiency equations vs the full scheme. The signed mean of all the difference values is 0.00078%, i.e, a positive number, suggesting that, statistically speaking, the sufficiency results are lower than the full projection scheme. The reason may be attributed to the greater number of degrees of freedom in the sufficiency equations. The absolute mean value, an important qualifier for our set of data is 0.00175%, certainly not a very large value. The maximum and minimum values and standard deviations of differences are also reasonable quantities (please refer to Table 2.14). From this analysis we may conclude that the dispersion of data for sufficiency as against projection is not high. In another set of comparisons for Schemes P and S, we have seen a consistent change in percentage correlation with the increase in the basis size for our theory (please refer to Table 2.15). There are no sudden jumps in error as evidenced by the small standard deviation. This is true for both the schemes and hence validates our expectation that there are no limitations in the description of excited states for our theory with increasing basis size. The mean and standard deviations are very similar for Schemes P and S indicating that invoking sufficiency does not affect the change of energy with increasing basis size.

The trends for accuracy as evidenced by difference from FCI values are the same

Table 2.3: **Ionized states of H_2O in cc-pVDZ basis**

Method	$^2B_1$	M-FCI	$^2A_1$	M-FCI	$^2B_2$	M-FCI
Scheme P	-75.806359	0.533	-75.731910	1.000	-75.555040	3.193
Scheme A	-75.804555	2.337	-75.731647	1.263	-75.556011	2.222
$COS-CC^b$	-75.804342	2.55	-75.731459	1.451	-75.556294	1.939
$SSCC^c$	-75.803116	3.776	-75.729324	3.586	-75.553028	5.205
$ROHF-CCSD^a$	-75.804255	2.637	-75.730282	2.628	-75.555214	3.019
$UHF-CCSD^a$	-75.804287	2.605	-75.730319	2.591	-75.555278	2.955
EOM-CC	-75.809345	-2.453	-75.734969	-2.059	-75.557381	0.852
FCI	-75.806892		-75.732910		-75.558233	

Geometry:O-H = 1.84345 a.u.; O-H-O = 110.6°

for UGA-QFMRCC and the parent UGA-SUMRCC. Results show a difference of the order of a mH. The UGA-QFMRCC predicts excitation energies which are consistently lower than the corresponding value obtained by taking an explicit difference of UGA-SUMRCC excited state energy and CCSD ground state energy. Due to the unitary group adapted description of our target state and use of projection equations, higher body G-blocks (three and four body) are involved. Thus, although the description of the ground and excited states are well-balanced in terms of ranks of the excitation operators, there exists a discrepancy at the block level. The use of projection equations necessitates the involvement of certain three and four body blocks which correspond to triples and quadruples as in CCSDtq [38]. These could implicitly contribute to an over-correlation of the excited state as against the ground state which is correlated at the purely CCSD level. The more or less consistent improvement over EOM-CCSD is most likely due to the greater incorporation of orbital relaxation.

We would like to draw the attention of the readers to the fact that the results in Secs. 2.4.1, 2.4.2 and 2.4.3 are somewhat improved from those reported in our first publication on UGA-SUMRCC [7] as a result of correcting a bug in the program. However, the conclusions regarding the trends in the numbers remain unaltered.

2.4.1 Electron Detached States

For electron detached states, the orbitals of the target state are the same as that of the ground state up to first order (Brillouin theorem). Scheme P with full orbital relaxation and Scheme A with considerably less relaxation are thus, expected to perform comparably. Our results validate this point.

Table 2.4: $^2\Pi_1$ **ionized state of HF in DZV and cc-pVTZ basis**

Method	DZV		cc-pVTZ
	$^2\Pi$	M-FCI	$^2\Pi$
Scheme P	-99.572602	1.391	-99.762090
Scheme A	-99.570133	3.860	-99.761351
ROHF-CCSD	-99.572847	1.1456	-99.760554
EOM-CC	-99.586255	-12.261	-99.763371
VUCCSD	-	-	-99.757401
FCI	-99.573993	-	-

Geometry:H-F = 1.7328 a.u.

Table 2.5: **Electron attached state of H_2O in cc-pVDZ basis**

Method	$^2A_1$	$^2B_2$
Scheme P	-76.073049	-76.001358
Scheme A	-76.072786	-76.000844
ROHF-CCSD	-76.072889	-
EA-EOM-CC	-76.073436	-76.001873

Geometry:O-H = 1.84345 a.u.; O-H-O = 110.6°

2.4.2 Electron Attached States

For electron attached state, the considerable difference in the orbitals of the reference and target states compel us to incorporate as much relaxation as possible.

2.4.3 Neutral Radicals

Neutral radicals can be treated as electron detached states of the corresponding anions or electron attached states of the corresponding cations. However, we must be careful to ensure that our chosen vacuum is single reference. We present results for $F^{\cdot}$, $NH_2^{\cdot}$, $OH^{\cdot}$ and $CH_3{}^{\cdot}$ as an electron detached states and $CH^{\cdot}$ as an electron attached state.

Table 2.6: **Ground State Energies of Neutral Radicals computed using UGA-SUMRCC. M-FCI denotes difference of the energy wrt FCI in mH**

Method	OH $^2\Pi$ M-FCI		CH$_3$ $^2\Pi$ M-FCI		F $^2\Pi$ M-FCI	NH$_2$ ^{2}B$_2$	CH $^2\Pi$ M-FCI
Basis	6-31G**	cc-pVTZ	DZ	cc-pVTZ	aug-cc-pVDZ	cc-pVTZ	cc-pVDZ
Scheme P	-0.713	-75.646977	-0.753	-39.773476	0.822	-55.803776	1.280
Scheme A	0.995	-75.646615	0.749	-39.773905	2.282	-55.803887	2.038
COS-CC [35]	-	-75.646612	0.644	-39.774322	4.500	-55.804092	-
SSCCSD [35]	-	-	1.08	-	-	-	-
ROHF-CCSD	2.083	-7.644768	1.805	-	0.716	-55.801152	2.519
EOM-CCSD	-4.54	-75.645004	-0.501	-39.752338	4.264	-55.785509	1.923
FCI	-75.546486		-39.644673		-99.55029		-38.382017

Geometry: [1] OH$^{\cdot}$: O-H=0.9697$\mathring{A}$; [2] $CH_3^{\cdot}$: C-H=2.06 a.u., H-C-H=120°; [3] $NH_2^{\cdot}$: N-H=1.024$\mathring{A}$, H-N-H=103.4°; [4] CH$^{\cdot}$: C-H=1.131$\mathring{A}$

2.4.4 Excited States

In the first set of tables we benchmark our UGA-SUMRCC theory against FCI and other comparable open-shell CC theories for excited states. Next we compare the performance of equations with sufficiency conditions with an over-parametrized excitation space against the projection equations with a linearly independent manifold of operators. Finally, we compare excitation energies obtained by explicit difference of excited state energies obtained from UGA-SUMRCC and a closed shell SRCC ground state and those by direct computation using UGA-QFMRCC.

Benchmark Studies of UGA-SUMRCC

Table 2.7: **Singlet excited states of water using DZV basis**

Method	$^1B_1$	M-FCI (mH)	$^1A_2$	M-FCI (mH)	$^1A_1$	M-FCI (mH)	$^1B_2$	M-FCI (mH)
Scheme P	-75.816863	1.399	-75.740235	1.819	-75.729277	1.461	-75.640250	3.152
Scheme S	-75.817596	0.666	-75.741435	0.619	-75.730500	0.238	-75.643499	-0.097
Scheme S$'$	-75.816489	1.773	-75.740798	1.256	-75.730253	0.485	-75.640936	2.466
EOM-CCSD	-75.821486	-3.224	-75.744183	-2.129	-75.733449	-2.711	-75.644781	-1.379
FCI	-75.818262	-	-75.742054	-	-75.730738	-	-75.643402	-

Geometry: O(0,0,0),H(0,±0.751155,-0.581606) in $\mathring{A}$

Table 2.8: **Triplet excited states of water using DZV basis**

Method	$^3B_1$	M-FCI (mH)	$^3A_2$	M-FCI (mH)	$^3A_1$	M-FCI (mH)	$^3B_2$	M-FCI (mH)
Scheme P	-75.845827	0.356	-75.759085	0.491	-75.763853	0.957	-75.688871	1.896
Scheme S	-75.845315	0.868	-75.758776	0.800	-75.763417	1.393	-75.689339	1.428
Scheme S′	-75.843689	2.494	-75.757756	1.820	-75.762718	2.092	-75.689800	0.967
EOM-CCSD	-75.849656	-3.473	-75.761222	-1.646	-75.767952	-3.142	-75.692649	-1.882
FCI	-75.846183	-	-75.759576	-	-75.764810	-	-75.690767	-

Geometry: O(0,0,0),H(0,±0.751155,-0.581606) in Å

Table 2.9: **Singlet and triplet excited states of HF using DZV basis**

Method	$^1\Pi$	M-FCI (mH)	$^3\Pi$	M-FCI (mH)
Scheme P	-99.580710	2.218	-99.603656	1.328
Scheme S	-99.581510	1.418	-99.604007	0.977
Scheme S′	-99.580383	2.545	-99.602908	2.076
EOM-CCSD	-99.591057	-8.130	-99.613134	-8.150
FCI	-99.582928	-	-99.604984	-

Geometry:H-F=1.40 a.u.

Table 2.10: **Singlet and triplet excited states of CH_2 using cc-pVDZ basis**

Method	$^1B_1$	M-FCI (mH)	$^1A_1$	M-FCI (mH)	$^3B_1$	M-FCI (mH)	$^3A_1$	M-FCI (mH)
Scheme P	-38.962073	0.275	-38.722847	1.545	-39.033638	-2.611	-38.742057	2.564
Scheme S	-38.961186	1.162	-38.723192	1.200	-39.031970	-0.943	-38.742228	2.393
Scheme S′	-38.962776	-0.428	-38.724279	0.113	-39.032367	-1.340	-38.741978	2.643
EOM-CC	-38.959034	3.314	-38.720011	4.381	-39.028531	2.496	-38.740466	4.155
FCI	-38.962348	-	-38.724392	-	-39.031028	-	-38.744621	-

Geometry: C(0,0,0),H(0,±0.87251,-0.67314) in Å

Table 2.11: **Singlet and triplet excited states of BH using cc-pVDZ basis**

Method	$^1\Pi$	M-FCI (mH)	$^3\Pi$	M-FCI (mH)	$^1\Sigma_1$	M-FCI (mH)	$^3\Sigma_1$	M-FCI (mH)
Scheme P	-25.105068	0.132	-25.169890	-1.299	-24.851627	-1.126	-24.914764	3.061
Scheme S	-25.103118	2.082	-25.167822	0.769	-24.850924	-0.423	-24.908551	9.274
Scheme S′	-25.104499	0.701	-25.169678	-1.087	-24.848211	2.290	-24.910691	7.134
EOM-CC	-25.102518	2.682	-25.166993	1.598	-24.847535	2.966	-24.913286	4.539
FCI	-25.105200	-	-25.168591	-	-24.850501	-	-24.917825	-

Geometry: B-H=2.3289 a.u.

Table 2.12: **Singlet and triplet excited states of CH^+ using cc-pVDZ basis**

Method	$^1\Pi$	M-FCI (mH)	$^3\Pi$	M-FCI (mH)
Scheme P	-37.886484	-0.358	-37.962947	-1.606
Scheme S	-37.886138	-0.012	-37.962014	-0.673
Scheme S′	-37.887068	-0.942	-37.963114	-1.773
EOM-CCSD	-37.883039	3.087	-37.959286	2.055
FCI	-37.886126	-	-37.961341	-

Geometry: C-H=2.137280 a.u.

Use of Non-redundant vs Redundant Excitations

Table 2.13: **Scheme S - Scheme P in mH**

Molecule	State	cc-pVDZ	cc-pVTZ	cc-pVQZ
HF	$^1\Pi$	-1.776	-1.889	-1.992
	$^3\Pi$	-0.959	-1.24	-1.258
H_2O	$^1B_1$	-2.751	-2.638	-2.656
	$^1A_2$	-1.689	-1.888	-2.206
	$^1A_1$	-2.197	-1.792	-1.639
	$^1B_2$	-2.234	-2.025	-1.977
	$^3B_1$	-0.959	-1.009	-1.049
	$^3A_2$	0.206	-0.077	-0.413
	$^3A_1$	-0.336	-0.343	-0.446
	$^3B_2$	0.111	-0.099	-0.332
CH_2	$^1B_1$	0.887	0.108	0.212
	$^3B_1$	1.668	0.529	0.316
CH^+	$^1\Pi$	0.346	0.858	2.653
	$^3\Pi$	0.933	1.016	1.77

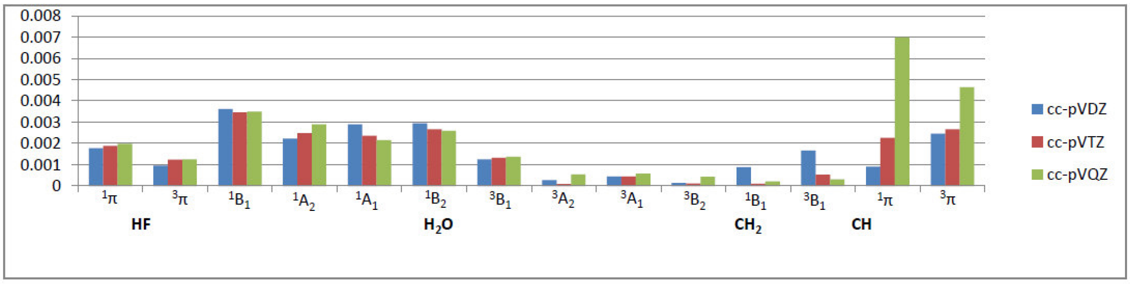

Figure 2.1: **Bar-chart showing absolute percent error of S vs P**

Table 2.14: **Statistical data for percent error of S vs P**

	$\frac{abs(S-P)}{P} * 100$	$\frac{(S-P)}{P} * 100$
Mean	0.00175	0.00078
S.D.	0.00143	0.00214
Max diff	0.00699	0.00362
Min diff	0.00010	-0.00699

Table 2.15: **Statistical data for correlation gain with increase in basis size**

	(CCT-CCD)/CCD *100		(CCQ-CCT)/CCT *100	
	UGA-SUMRCC(P)	UGA-SUMRCC(S)	UGA-SUMRCC(P)	UGA-SUMRCC(S)
Mean	0.1271	0.1274	0.0625	0.0621
S.D.	0.0198	0.0200	0.0037	0.0045
Max gain	0.1456	0.1453	0.0690	0.0690
Min gain	0.0779	0.0777	0.0553	0.0532

Quasi-Fock MRCC

Table 2.16: **Singlet Excitation Energies (ΔE) of water in DZV basis**

Method	Scheme	$^1B_1$	$^1A_2$	$^1A_1$	$^1B_2$
UGA-QFMRCC	Scheme P	0.322132	0.398896	0.409569	0.498643
	Scheme S	0.321385	0.397601	0.408268	0.494970
	Scheme S′	0.322443	0.398175	0.408680	0.497743
UGA-SUMRCC	Scheme P	0.322465	0.399093	0.410051	0.499078
	Scheme S	0.321732	0.397893	0.408828	0.495829
	Scheme S′	0.322839	0.398530	0.409075	0.498392
EOM-CCSD		0.317842	0.395145	0.405879	0.494547
FCI		0.322704	0.398912	0.410228	0.497564

Geometry: O(0,0,0),H(0,±0.751155,-0.581606) in Å

Table 2.17: **Triplet Excitation Energies (ΔE) of water in DZV basis**

Method	Scheme	$^3B_1$	$^3A_2$	$^3A_1$	$^3B_2$
UGA-QFMRCC	Scheme P	0.293259	0.380042	0.375226	0.449528
	Scheme S	0.293661	0.380219	0.375303	0.448740
	Scheme S′	0.294947	0.380984	0.375299	0.447629
UGA-SUMRCC	Scheme P	0.293501	0.380243	0.375475	0.450457
	Scheme S	0.294013	0.380552	0.375911	0.449989
	Scheme S′	0.295639	0.381572	0.376610	0.449528
EOM-CCSD		0.289672	0.378106	0.371376	0.446679
FCI		0.294783	0.381390	0.376156	0.450199

Geometry: O(0,0,0),H(0,±0.751155,-0.581606) in Å

Table 2.18: **Singlet and Triplet Excitation Energies (ΔE) of HF in DZV basis**

Method	Scheme	$^1\Pi$	$^3\Pi$
UGA-QFMRCC	Scheme P	0.493533	0.470572
	Scheme S	0.492702	0.470053
	Scheme S′	0.493822	0.471018
UGA-SUMRCC	Scheme P	0.493059	0.470113
	Scheme S	0.492259	0.469762
	Scheme S′	0.493386	0.470861
EOM-CCSD		0.482712	0.460635
FCI		0.492826	0.470770

Geometry:H-F=1.40 a.u.

Table 2.19: **Singlet and Triplet Excitation Energies (ΔE) of BH in cc-pVDZ basis**

Method	Scheme	$^1\Pi$	$^3\Pi$
UGA-QFMRCC	Scheme P	0.107971	0.043900
	Scheme S	0.110134	0.046459
	Scheme S$'$	0.106510	0.043683
UGA-SUMRCC	Scheme P	0.109262	0.044440
	Scheme S	0.111212	0.046508
	Scheme S$'$	0.109831	0.044652
EOM-CCSD		0.111811	0.047337
FCI		0.113699	0.047626

Geometry: B-H=2.3289 a.u.

Table 2.20: **Singlet and Triplet Excitation Energies (ΔE) of CH^+ in cc-pVDZ basis**

Method	Scheme	$^1\Pi$	$^3\Pi$
UGA-QFMRCC	Scheme P	0.114014	0.037854
	Scheme S	0.114647	0.039080
	Scheme S$'$	0.112453	0.037271
UGA-SUMRCC	Scheme P	0.115143	0.038680
	Scheme S	0.115489	0.039613
	Scheme S$'$	0.114559	0.038513
EOM-CCSD		0.118588	0.042341
FCI		0.117478	0.042263

Geometry: C-H=2.137280 a.u.

Table 2.21: **Singlet and Triplet Excitation Energies (ΔE) of CH^+ in $14\sigma 5\pi 1\delta$ basis [39]**

Method	$^1\Pi$
UGA-QFMRCC (P)	0.115030
CC3	0.119068
STEOM-CC	0.116128
EOM-CCSD	0.119803
FCI	0.118700

Geometry:Bond length=2.13713 a.u.

Table 2.22: **Excitation Energy of water**

Method	$^1B_1$		$^1A_2$		$^3B_1$		$^3A_2$	
	Sadlej	ANO	Sadlej	ANO	Sadlej	ANO	Sadlej	ANO
UGA-QFMRCC (P)	0.274858	0.277845	0.339898	0.342474	0.258286	0.261563	0.331370	0.334170
EOM-CCSD	0.272035	0.280795	0.336538	0.345359	0.257249	0.266374	0.330241	0.339266
VUMRCC	0.276318				0.264889			
Experiment	0.275252^a		0.334416^b		0.257245^c		0.338091^c	
					0.264595^b		0.334416^d	

Geometry:O(0,0,0),H(0,±0.7566,-0.5858) in Å
a. Ref. [40]; b. Ref. [41]; c. Ref. [42]; d. Ref. [43]

Table 2.23: **Singlet Excitation Energies (ΔE) of C_2H_2 in aug-cc-pVDZ basis**

Method	$1^1\Pi$	$2^1\Pi$	$1^3\Pi$	$2^3\Pi$
UGA-QFMRCC (P)	0.295153	0.309933	0.290207	0.302958
EOM-CCSD	0.304774	0.318854	0.309009	0.314472
Experiment	0.299872^a	0.331109^a	0.296199	0.314206

Geometry:C(0.000,0.000,1.66245),H(0.000,0.000,0.60085) in Å
a. Ref.([44])

2.4.5 An Investigative Study on LiH

In the ground state, equilibrium bond length of LiH is 1.6$\AA$. We have chosen cc-pVDZ basis for this molecule. Our model space contains 2 model functions of A_1 symmetry and two others of B_1 and B_2 symmetry. This choice of model space provides results which are in good agreement with the FCI values. But the results with one dimensional model space for A_1 is a bit away from FCI suggesting the multi-reference character of the state $1^1\Sigma$. As the results overshoot the FCI values, we can predict that the state

Table 2.24: **Singlet excited states of LiH using cc-pVDZ basis in its ground state equilibrium geometry**

Method	Dim. of model sp.	1^1A_1	M-FCI (mH)	$^1B_1$	M-FCI (mH)	2^1A_1	M-FCI (mH)
Scheme P	1	-7.889919	-2.607	-7.850524	-0.535	-	-
Scheme P	2	-7.889105	-1.793	-	-	-7.778169	-1.942
EOM-CC	-	-7.887235	0.077	-7.849942	0.047	-7.776210	0.017
FCI	-	-7.887312	-	-7.849989	-	-7.776227	-

Table 2.25: **Triplet excited states of LiH using cc-pVDZ basis in its ground state equilibrium geometry**

Method	Dim. of model sp.	1^3A_1	M-FCI (mH)	$^3B_1$	M-FCI (mH)	3^1A_1	M-FCI (mH)
Scheme P	1	-7.904557	-3.336	-7.862832	0.411	-	-
Scheme P	2	-7.901738	-0.517	-	-	-7.805628	-1.776
EOM-CC	-	-7.901194	0.027	-7.863213	0.03	-7.803838	0.014
FCI	-	-7.901221	-	-7.863243	-	-7.803852	-

$1^1\Sigma$ contains some contribution of the ground state in its description. Otherwise, the trend in results under different schemes is quite trustworthy to suggest that we can employ the most computationally efficient scheme for our subsequent studies.

Another study we undertake here is to study the role of choosing linearly independent (LIN) cluster operators. We have chosen the lowest $^3\Sigma$ state of LiH for our investigations. In Table 2.26 we enlist the classes of cluster operators chosen in the various schemes we have used. The difference of the energies computed by our UGA-SUMRCC method with FCI along the PES of the $^3\Sigma$ state of LiH has been plotted in Fig. 2.2 for these schemes. We find that the parallelity of the error plot is maximum when proper LIN cluster operators are used (green line). As expected, discarding the cluster operators which are dependent altogether results in a loss of correlation energy thereby increasing the difference with respect to FCI (red line). The destabilizing effect of linear dependence in the excitation manifold is also evident (black line). We may thus infer that choosing a LIN set of operators is advantageous from the point of view of stability and consistency of the computed energies.

Table 2.26: **Choice of the operator manifold for computing the PES of the lowest $^3\Sigma$ state of LiH**

Curve	E_i^a	E_{iu}^{ua}	E_{iv}^{va}	E_u^a	E_{uv}^{va}	E_{vu}^{ua}	E_i^u	E_{iv}^{vu}	E_{iu}^{uv}
Black	Y	Y	Y	Y	Y	Y	Y	Y	Y
Red	Y	N	N	Y	N	N	Y	N	N
Green	Y	Y	Y	Y	N	N	Y	N	N

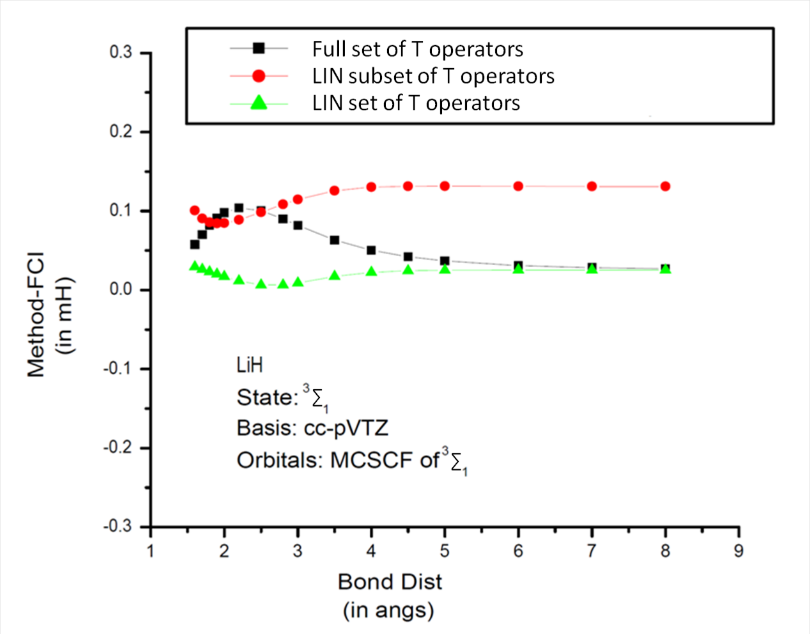

Figure 2.2: PES of the lowest $^3\Sigma$ state of LiH using various choices of excitation operators (see Table 2.26)

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Chapter 3

Orbital Relaxation on Ionization and Excitation in the Presence of Electron Correlation: A Study on Core Electrons

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3.1 Introduction

It is found that the Koopman's IP [1] does not match well with experimental IPs such as from X-ray photoelectron spectroscopy for core electron ionizations. On the other hand, taking explicit difference of state energies, ie. by the so-called ΔSCF methods, gives a much better description. For example, for the N 1s ionization in NO, ΔSCF predicts an IP of 409.22 eV (at the basis set limit) against the experimental value of 410.3 eV [2]. The Koopman's theorem result is above 430 eV! This observation at the mean-field level indicates that the orbitals for the GS and ionized state differ greatly for core-electron ionizations and using proper orbitals is vital. On the other hand, for correlated descriptions the use of common orbitals for correlating the ground and ionized state is very attractive since it allows a more balanced description of the differential correlation which accompanies ionization or excitation and allows the common correlation terms of the two states concerned to cancel out giving better energy differences. These two apparently incompatible requirements may be mutually resolved by formulating a theory with high implicit orbital relaxation making use of the Thouless theorem [3]. This is the path we have followed in our formulation.

As shown by Thouless, action of an exponential operator with single excitations acting on a determinant is equivalent to creating another determinant with rotated orbitals. Thus, for SRCC, T_1 represents orbital relaxation under correlation of electrons. In an MRCC framework when the targeted state belongs to a valence sector different from that for which the orbitals have been optimized, the T_1 operators also account for orbital relaxations for this change. For example what we deal with in this chapter is the computation of energies of core-electron ionized and excited states using the optimized orbitals of the neutral closed shell ground state. In this case an appropriate choice of the wave operator for the ionized/excited state should not only ensure a proper modeling of the electron correlation of the ionized/excited state but also sufficient orbital relaxation. In fact the role of orbital relaxation becomes important whenever different charge sectors are involved such as in the case of ionized states, though the extent of such relaxation becomes very prominent for core electron ionization or even, excitation. Magnitude-wise the valence electron ionizations and excitations are accompanied by less orbital relaxation but it needs to be addressed because, clearly, when the orbital relaxation is not as severe as for core electron ionization/excitation, it is still as important as the differential correlation and must be incorporated. It would thus be be beneficial to have a theory which takes both into account but in an unbiased fashion. In our UGA-SUMRCC and UGA-QFMRCC theories we propose to take care of this by a coupled modeling of orbital relaxation and correlation via the Thouless transformation induced on ionized/excited states with neutral orbitals which is inherent in the normal-ordered multi-exponential Ansätz we have used.

3.2 Theoretical Considerations

As mentioned before, our UGA-SUMRCC and UGA-QFMRCC theories are spin-free. This is achieved by unitary group adaptation of the T operators which are labeled by spatial orbitals of a common closed shell vacuum and the resulting problem of non-commutativity of the T_μ/S_μs is alleviated by a normal-ordering of the multi-exponential Ansätz with respect to a common closed shell vacuum. A problem with such an approach is that the orbitals to be used are for one function which may not be one of the model functions or even of the same valence sector making it essential to have a mechanism for correction of orbitals in the wave operator Ansätz. In the theories formulated in this thesis we have chosen to use the Thouless parametrization for orbital relaxation implicit in the exponential Ansätz of coupled-cluster to take care of the orbital relaxation both due to ionization/excitation and due to correlation. These two effects are, however, intermingled and cannot be separated out numerically although one may analyze the mechanism by which they are introduced. Before we embark on this analysis, we may point out that, in coupled-cluster a Thouless parametrization with e^{T_1} is only on the ket function, the bra function remains unrelaxed. This feature carries through into our formalisms but our results indicate that this is sufficient, at least for the molecules we have studied. A fuller parametrization for relaxation of both the bra and ket functions would have been a unitary transformation of the orbitals via e^{σ} where σ is an anti-Hermitian operator. However, σ is a combination of excitation and de-excitation operators, $\sigma = T - T^{\dagger}$, making them non-commuting. This makes such a theory intractable due to the occurrence of non-terminating series of operators. This is useful only when orbital relaxations to a given order under some external perturbation needs to be evaluated such as during the solution of the coupled perturbed Hartree-Fock (CPHF) equations for computation of molecular properties.

If the non-commutativity of the T_μs is retained in the Ansätz (ie. no additional normal ordering of the Ansätz is done) the T-operators must be allowed to contract among themselves leading to interminable chains of T operators in both the direct and the coupling terms. A so-called *double-curly* Ansätz, $\{\{e^{T_\mu}\}\}$ was developed by Datta and Mukherjee [4, 5] where contractions among certain types of operators were allowed with suitable evaluation of combinatoric factors leading to the Combinatoric Open-Shell Coupled Cluster (COS-CC) theories. In this case, the evaluation of the chains of one-body excitation inducing operators results in full clustering analogous to a spinorbital based theory and a high degree of Thouless relaxation is possible. However, the evaluation of chains of operators and the determination of the corresponding combinatoric factors is more involved than a theory using the normal-ordered cluster Ansätz in UGA-SUMRCC theory. The μ-dependence of the operators T_μ and S_μ allows us to delete valence spectator excitations and thus allows full exponential structure of the wave operator for all those excitations which do not involve valence destructions. This feature alone makes the UGA-SUMRCC theory worth exploring. Assuming we are to use the normal ordered Ansätz, we can overcome the loss of clustering to a considerable extent by clubbing together certain operators such that the valence destruction containing operators which are proportional to lower body operators do not occur explicitly but their effect is implicitly taken to all powers of the lower body operator. For example, contributions from the composites G_i^a and G_{iA}^{aA} (whose nature has been discussed in Chp. 2) are added together and the sum contributes to the equation for T_i^a. The operator T_{iA}^{aA} is discarded. However, operators like T_{iA}^{Aa},T_i^I and T_A^a terminate at linear power due to their inability to contract with each other unlike in COS-CC. We will come back later in this section to this issue in our analysis of the structure of our theory vis a vis. other comparable theories. This would apparently appear to be a great loss of relaxation but interestingly, the *coupling terms* of Eqs. 2.25 and 2.47 which are significantly different in structure from the corresponding terms of the spinorbital-based theories reintroduces some higher powers of these operators through the contraction of the T_μs with $W_{\nu\mu}$ which contains T_μs.

Since the formulation of our UGA-QFMRCC is tangentially related to the Fock-space MRCC (FS-MRCC) [6, 7, 8], Fock-space Eigenvalue Independent Partitioning (FS-EIP) [9] and the Similarity Transformed Equation of Motion CC (STEOM-CC) theory [10, 11, 12], we think that a comparative study of these theories will serve to better elucidate the mechanism of orbital relaxation in this class of theories. The arguments with regard to the S_μ operators in UGA-QFMRCC essentially hold true for the T_μ operators in UGA-SUMRCC as well.

All the theories including our UGA-QFMRCC use the factorized cluster Ansätz for the wave operator of the excited state:

$$\Omega = e^T \Omega_v \tag{3.1}$$

where e^T is the wave operator for the ground state in the CC form and Ω_v introduces the effects of valence correlation, core-valence interaction and orbital relaxation/differential correlation. The physical content of Ω_v is different in the four theories leading to the effective Hamiltonian, $\bar{H}_{eff}$ being different for the three theories although the ground state energy contribution is exactly the same for the same truncation scheme for the GS. The FS-MRCC, the FS-EIP and the STEOM-CC all invoke the concept of valence universality [6] and express Ω_v as:

$$\Omega_v = \{e^S\} \tag{3.2}$$

where S consists of cluster operators of different valence sectors: $S = S^{(0,1)} + S^{(1,0)} + S^{(1,1)}$. $S^{(m,n)}$ are the valence cluster operators involving destruction of 'm' holes and 'n' electrons occupying the mh and np active orbitals in the model functions. In the FS-MRCC, the $S^{(1,0)}$ and $S^{(0,1)}$ amplitudes are solved to get the information on the IP and EA sectors respectively. The additional correlation, including the dispersion interaction between the active hole and particle for the (1,1) sector is taken care of by the $S^{(1,1)}$ cluster amplitudes. In the FS-EIP, the Bloch equation for every valence sector is cast into an eigenvalue equation obtained in the union space of $\{\phi_\mu^{(m,n)}\}$, and the set $\{\chi_\mu^{l(m,n)} \equiv \varepsilon_\mu^{l(m,n)} \phi_\mu^{(m,n)}\}$ where $\{\phi_\mu^{(m,n)}\}$ denotes the set of model functions for the (m,n) sector and the set $\{\chi_\mu^{l(m,n)}\}$ are the virtual functions obtained by the action of excitation operators $\varepsilon_\mu^{l(m,n)}$ on $\phi_\mu^{(m,n)}$. In STEOM-CC, a technique similar to FS-EIP is used with the proviso of an approximation that the $S^{(1,1)}$ amplitudes are ignored altogether. In our UGA-QFMRCC, all the cluster operators are for the (1,1) sector and there is no hierarchical build-up through the (0,1) and (1,0) sectors to the (1,1) sector. An advantage of FS-EIP or STEOM-CC, as currently implemented, lies in that the (1h, 0p) and (0h,1p) valence sector equations can be exactly cast as a matrix eigen-problem, enabling easy and intruder-free evaluation of S-amplitudes. Although in principle, our UGA-QFMRCC also can be cast as a matrix eigen-problem, thereby obviating intruders in a similar manner, we have not implemented such a strategy yet. We tend to look upon the transcription of the set of Bloch equations to the matrix eigen-problem as a technique to handle intruders.

The strength of the UGA-QFMRCC theory lies in the model-function dependence of the S-amplitudes (the so-called μ dependence), which eliminates altogether the artificial use of higher rank S-amplitudes with direct spectator scatterings. This in itself ensures that all the S-amplitudes have knowledge of all the valence occupancies of the model functions. If we refer to the Ansätz of our wave operator in Eq. 2.34, the factorized Ansätz $e^T\{e^{S_\mu}\}$ for the component Ω_μ of the wave operator acting on ϕ_μ ensures that not only the ground state dressing via e^T of the Hamiltonian makes the direct computation of excitation energy possible but also it allows us to use S-amplitudes involving excitations only while incorporating the involvement of all the active holes and particles present in ϕ_μ. As an example, an operator S_μ inducing excitation from $i \to a$ for a function ϕ_μ with active occupancy (I,A), subsumes in it interaction with I and A separately as spectators as also the interactions where I and A are both involved.

As depicted in (Fig. 3.1) single excitations like E_i^a, E_{iA}^{aA} and E_{iA}^{Aa} among others are involved in correction of orbitals for model spaces where A is an active virtual orbital (say, for a 1p or 1h-1p model space). In a FS-MRCC or FS-EIP/STEOM-CC, E^{aA}_{iA}, E^{Aa}_{iA}, E^{aI}_{iI} and E^{Ia}_{iI} which are responsible for orbital relaxation due to change in valence occupancy are present up to linear power only while in UGA-QFMRCC, the set of operators E^{a}_{i}, E^{aA}_{iA}, E^{aI}_{iI}, E^{aIA}_{iIA} and E^{aAI}_{iIA} are clubbed together as $\epsilon_i^{a(\mu)}$ (denoted with bold vertices in (Fig. 3.2) which occurs to all powers. Hence, more physics is incorporated in UGA-QFMRCC on two counts: (a) knowledge of the S-amplitudes regarding the valence occupancies I and A and (b) a full exponential involving $S_{\mu i}^{\;\;a}$ (with $\phi_\mu \equiv \phi_I^A$). When E^{Aa}_{iA} is LIN with E^{a}_{i}, however, it occurs up to linear power even in UGA-QFMRCC. The correlation on the other hand is incorporated by the two body excitation operators and differential correlation by three body operators with direct and exchange spectators as in Fig. 3.2. Thus, in FS-MRCC or FS-EIP/STEOM-CC, a CCSD truncation scheme has no such differential correlation operators while the UGA-QFMRCC easily incorporates the direct spectator contributions to all orders. The exchange spectator blocks implicitly contribute in the projection equations. Other than spectator scatterings, orbital relaxation and correlation relaxation also occur in presence of multiple valence occupancies. In order to fully include all such contributions, it would be necessary to use up to (m+n+2) rank operators for an (m,n)-valence sector such as in Fig. 3.3 which is not a practical possibility in FS-

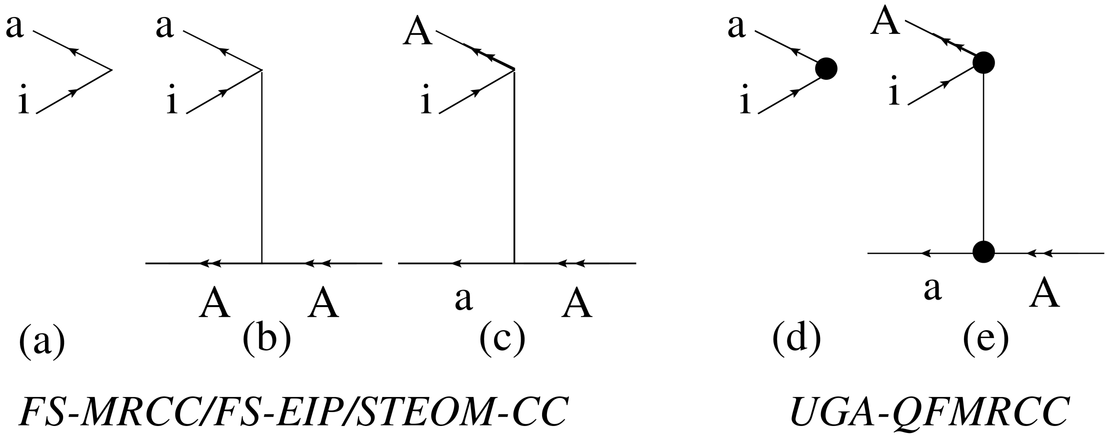

Figure 3.1: FS-MRCC/FS-EIP/STEOM-CC [(a),(b)] vs UGA-QFMRCC [(d),(e)]- Orbital relaxation diagrams: Note that for the (0,1) sector and the target (1,1) sector, the operator in (b) from normal-ordered Ω_v terminates at linear power while (d) subsumes (a) and (b) and thus, occurs to all powers. Following the usual convention, inactive lines are denoted by single arrows and the active lines are denoted by double arrows. The filled circle vertex in Figs. (d) and (e) depict the model space dependence of the inactive excitation operator of S_μ.

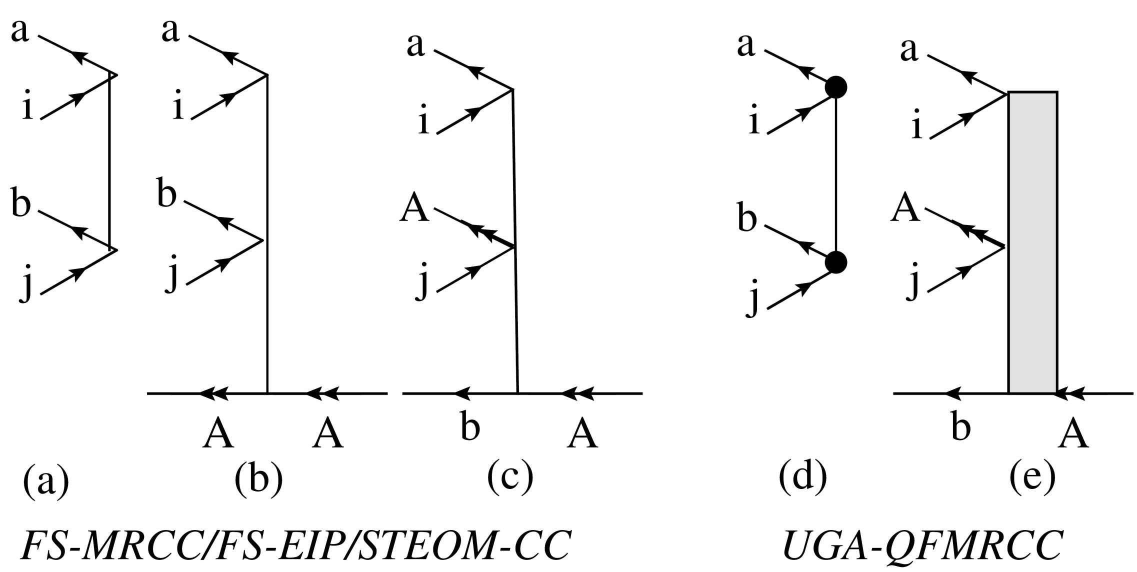

Figure 3.2: FS-MRCC/FS-EIP/STEOM-CC vs UGA-QFMRCC-Differential correlation:Note that for the (0,1) sector, the operators (b) and (c) from normal-ordered Ω_v are necessary for introducing differential correlation but are absent in a singles-doubles truncation while (d) subsumes (a) and (b) and thus, occurs to all powers. The operator, (c) is absent in UGA-QFMRCC but some implicit contribution through the G-block shown in (e) is possible.

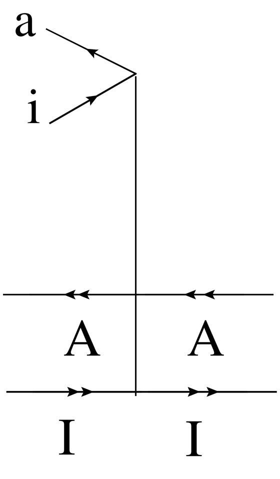

Figure 3.3: FS-MRCC/FS-EIP/STEOM-CC vs UGA-QFMRCC-Orbital relaxation for the (1,1) sector would, in principle require such a three-body operator from a normal-ordered Ω_v which is implicitly present in the $T_{\mu_i^a}$ of our UGA-QFMRCC

MRCC/FS-EIP/STEOM-CC with spectator scattering of 'm' holes and 'n' particles in both direct and exchange modes. However, the direct spectator scatterings in the FS-MRCC can be subsumed in UGA-QFMRCC with low body excitation operators labeled by the CSF index, μ, and such operators can be treated to all powers. The operators with some exchange spectator scatterings would still be having higher ranks than just the excitation ranks, but - unlike in the FS-MRCC/ FS-EIP/ STEOM-CC - μ dependence via inclusion of higher body blocks would not necessitate the inclusion of all the spectator labels. Some other excitations like E_i^I and E_A^a will terminate at the linear power in both the theories. If we ignore three and higher body excitations (exchange spectators, in particular), in FS theories they then never appear in the Bloch equation. In contrast, although the three/four body S_μs also do not appear in UGA-QFMRCC, the corresponding blocks do, enriching the physical content implicitly in UGA-QFMRCC. In STEOM-CC, as mentioned above, one ignores the $S^{(1,1)}$ amplitudes and it would miss the dispersion interaction in the wave function. Since our working equations have G-blocks with I and A both interacting, the dispersion interaction is incorporated. Inclusion of such multiple spectators becomes particularly relevant for the description of differential correlation accompanying excitation. We can simply introduce μ-dependent double excitations of the type $ij \rightarrow ab$ while in EIP/ STEOM-CC we would need at least a three-body operator with spectator active scattering or even a four-body operator with the pairs of I and A. Absence of this differential correlation in a truncated CCSD scheme is evident in the computed energies from EIP or STEOM-CC vis-a-vis UGA-QFMRCC. This is a general advantage of any theory based on or derived from the Jeziorski-Monkhorst Ansätz as against the Valence-Universal Ansätz. Moreover the Quasi-Fock formalism has cluster amplitudes for just the (0,0) and (1,1) sectors, thereby, bypassing entirely the necessity of having to go through the 1h-0p and 0h-1p sectors before reaching the target, 1h-1p sector. The number of cluster amplitudes in UGA-QFMRCC is thus less than that in EIP or STEOM-CC to include equivalent physics, which is further enhanced by the possibility of the appearance of all powers of S_μ which do not have exchange spectators. This would be best demonstrated in situations where orbital relaxation is very high such as core electron ionization and excitation. Preliminary investigations indicate that UGA-QFMRCC is considerably better than EOM-CC in these cases, although COS-CC [4] is better, as expected, though only marginally so.

Another allied and widely applied theory is SAC-CI [13, 14] which uses an exponential Ansätz for describing the correlation of the ground state adapted to the correct spin and spatial symmetry and a linear, CI-like Ansätz for generating the ionized/excited states of interest. It is structurally very much allied to the CC-LRT [15, 16, 17, 18] or EOM-CC [19, 20, 21, 22] methods (they differ in approximations used, viz. in details but not fundamentally). One of its variants, SAC-CI (R) [23, 24] uses orbitals of the ground state HF function. Another variant, SAC-CI (OR) [25], takes the orbitals of the core-ionized state in a similar setting. The SAC-CI for core ionized/excited states require higher order operators for reasonable accuracy. These higher body operators simulate the powers of h-p excitations which are absent in a SD truncation scheme of a linearized ionization/excitation operator. The corresponding higher order IP- and EA-EOM-CC theories have also been studied [26, 27]. Our results show that, using only up to double excitations we have been able to match or even supersede the accuracy of SAC-CI (R) using up to triple excitation operators.

3.3 The Role of Relativity

Core electrons feel the presence of the nuclear charge of the atom more strongly than the inner or outer valence electrons and hence, move faster. For example, the 1s electron of even a medium-heavy atom like Zn has a velocity of approximately 17% of light ! This would necessitate a relativistic treatment of the electron for even reasonable quantitative accuracy. However, for up to medium-heavy nuclei, the relativistic effect is mostly confined to the kinetic energy operator. This is known as the scalar relativistic effect. Of course, with the increase of the nuclear charge of the atom from which the core electron is ionized/excited, spin-dependent relativistic effects start getting important.

While it is possible to treat relativistic effects perturbatively [28], a fully relativistic treatment of the electron requires that we abandon the Schrödinger equation in favor of the Dirac equation. The explicit time-independent Dirac equation may be written as:

$$\hat{H}\psi = c\alpha \cdot (-i\hbar\nabla + e\mathbf{A})\psi + \beta mc^2\psi + \hat{V}\psi = E\psi; \quad \hat{V} = -e\phi \tag{3.3}$$

where, α and β are the Dirac matrices composed of the Pauli spin matrices, σ, and the 2×2 unit matrix I_2.

$$\alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix}; \quad \beta = \begin{bmatrix} I_2 & 0 \\ 0 & -I_2 \end{bmatrix}. \tag{3.4}$$

The other symbols have their usual meanings. Owing to the 4×4 α and β matrices, the wave functions obtained as a solution to Eq. 3.3 are represented by 4-component vectors with pairwise large and small components for up and down spins, ie. ψ_L^α, ψ_L^β, ψ_S^α and ψ_S^β for a free electron. The pair of large and small components for both spins are called 2-component spinors or bispinors and are related to the Pauli spinors. It is also possible to work with 2-component wave-functions by an exact transformation of the 4-component Dirac equation to an effective 2-component equation called in literature as X2C [29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41].

For an electron in a molecule, the weak magnetic fields generated by the nuclei may be safely neglected and we may forget the vector potential, A, in the Hamiltonian. The scalar potential, ϕ, is simply the Coulomb potential of the nuclei and electrons. These considerations lead to the Dirac-Coulomb Hamiltonian,

$$\hat{H}_{DC} = \sum_{i=1}^{n} \hat{h}_D(i) + \sum_{i<j}^{n} \frac{1}{r_{ij}} + \sum_{I<J}^{N} \frac{Z_I Z_J}{r_{IJ}} \tag{3.5}$$

where, $\hat{h}_D$ is the one electron Dirac operator in the molecular field of the nuclei (I,J, etc.),

$$\hat{h}_D = \beta mc^2 + c(\alpha \cdot \mathbf{p}) + \hat{V}_{eN}. \tag{3.6}$$

Though this Hamiltonian is not Lorentz invariant, and contains no relativistic treatment of electron-electron interactions, it is sufficient for our purposes as we work in the frame of the Born-Oppenheimer approximation [42] and we are only interested in the relativistic behavior through the kinetic energy term which is the most important for medium-heavy atoms. Approximating the electron-electron Coulomb interaction as a mean-field, one is led to the Dirac-Fock or Dirac-Hartree-Fock (DHF) theory exactly analogous to the non-relativistic Hartree-Fock theory. A solution of the DHF equation leads to both positive energy solutions for the electronic states and negative energy solutions. This indicates that a simple variational principle cannot be used for optimizing the mean-field function and one must employ the 'minimax' principle to avoid variational collapse.

A somewhat simpler, and computationally more attractive approach for core ionization and excitation studies, especially in conjunction with our spin-free MRCC theories, is to start out with the spin-free part of the Dirac-Coulomb Hamiltonian, and compute the positive energy orbitals via a minimax principle to get the spin-free Dirac-Fock orbitals. The separation of spin-free and spin-dependent terms is possible in the Dirac equation as shown by Dyall [43] by a change of metric suggested earlier by Kutzelnigg [28],

$$\begin{bmatrix} \psi_L \\ \psi_S \end{bmatrix} \rightarrow \begin{bmatrix} \psi_L \\ \phi_L \end{bmatrix} \tag{3.7}$$

with

$$\psi_S = \frac{(\sigma \cdot \mathbf{p})}{2mc} \phi_L. \tag{3.8}$$

The Dirac equation, Eq. 3.3, then, splits up into two coupled equations involving only the kinetic energy operator, $\hat{T} = \frac{(\sigma\cdot\mathbf{p})^2}{4m^2}$ as the coupling operator:

$$\begin{bmatrix} \hat{V} & \hat{T} \\ \hat{T} & \{\frac{(\sigma\cdot\mathbf{p})\hat{V}(\sigma\cdot\mathbf{p})}{4m^2c^2} - \hat{T}\} \end{bmatrix} \begin{bmatrix} \psi_L \\ \phi_L \end{bmatrix} = E \begin{bmatrix} 1 & 0 \\ 0 & \frac{\hat{T}}{2mc^2} \end{bmatrix} \begin{bmatrix} \psi_L \\ \phi_L \end{bmatrix} \tag{3.9}$$

The Hamiltonian corresponding to Eq. 3.3 can be separated into a spin-dependent and a spin-free part as given below:

$$H_{DC}^{sf} = \begin{bmatrix} V & T \\ T & \frac{\mathbf{p}\hat{\mathbf{V}}\cdot\mathbf{p}}{4m^2c^2} \end{bmatrix} \tag{3.10}$$

$$H_{DC}^{sd} = \begin{bmatrix} 0 & 0 \\ 0 & -\frac{i\sigma\cdot(\mathbf{p}\hat{\mathbf{V}}\times\mathbf{p})}{4m^2c^2} \end{bmatrix} \tag{3.11}$$

To arrive at this separation, the following identity has been used:

$$(\sigma\cdot\mathbf{p})\hat{V}(\sigma\cdot\mathbf{p}) = (\sigma\cdot\mathbf{p})(\sigma\cdot\hat{\mathbf{V}}\mathbf{p}) = \mathbf{p}\cdot\hat{\mathbf{V}}\mathbf{p} - i\sigma\cdot(\mathbf{p}\times\hat{\mathbf{V}}\mathbf{p}) \tag{3.12}$$

We use the spin-free DHF (SF-DHF) function as the starting point for incorporation of electron correlation using our set of UGA-MRCC theories. Upto atoms with medium nuclear charges, the scalar relativistic contributions dominate and in the orbitals obtained from the spin-free DHF theory they are already incorporated. An additional advantage is that the functions, ψ_L and ϕ_L may be expanded in the same finite basis set. The exact 2-component analogue of the SF-DHF theory was also developed and is called the SF-X2C [44, 45, 46, 30, 32, 47, 48, 37, 35, 49] theory. Our studies focus on the innermost core orbital, ie. the 1s orbital where there is no spin-orbit coupling and the dominant relativistic effect is the modification of the kinetic energy. We have undertaken to study the ionization and excitation of the core 1s electron in this chapter, and will compare the NR and relativistic (R) results against experimental values to assess the importance of this simple relativistic effect. The inclusion of spin-orbit coupling as a perturbation on the spin-free function is eminently possible and several studies [50, 51] indicate that this is a good approach at least for medium-heavy elements.

3.4 Molecular Investigations

3.4.1 Relative Orbital Relaxation for Different Theories

The relative amounts of orbital relaxation achievable by different theories when the Hamiltonian used for the variational optimization of the orbitals is different from the actual Hamiltonian used in the theory (ie. all correlated theories) may be demonstrated by starting out with different sets of orbitals obtained using different Hamil-

Table 3.1: $BeH^{\cdot}$ **radical in ANO basis**

Method	Orbitals Used	State Energy	M-FCI
UGA-SUMRCC (P)	HF orbitals of BeH^-	-15.204797	0.834
UGA-SUMRCC (P)	HF orbitals of BeH^+	-15.204667	0.964
UGA-SUMRCC (P)	ROHF orbitals of $BeH^{\cdot}$	-15.204481	1.150
UGA-SUMRCC (T)	HF orbitals of BeH^-	-15.205284	0.347
UGA-SUMRCC (T)	HF orbitals of BeH^+	-15.204241	1.390
UGA-SUMRCC (T)	ROHF orbitals of $BeH^{\cdot}$	-15.205041	0.590
SU-COSCC [4]	HF orbitals of BeH^-	-15.205360	0.270
SU-COSCC [4]	ROHF orbitals of $BeH^{\cdot}$	-15.205759	-0.128
EOM-CCSD	HF orbitals of BeH^-	-15.201809	3.8218
EOM-CCSD	HF orbitals of BeH^+	-15.204748	0.8828
ROHF-CCSD	ROHF orbitals of $BeH^{\cdot}$	-15.204798	0.833
FCI	-	-15.205631	

tonians and comparing the energies obtained. The less sensitive the energy is to the nature of the starting orbital, the more the capacity for orbital relaxation of the theory. We have chosen the doublet BeH radical at its equilibrium bond length of 1.32Åfor our demonstration. We use three sets of starting orbitals, viz. those optimized for the BeH$^+$ cation, BeH$^-$ anion and the ROHF orbitals of the BeH$^{\cdot}$ itself. The results obtained in an ANO triple zeta basis are presented in Table 3.4.1. As expected SU-COSCC incorporates much higher orbital relaxation than our UGA-SUMRCC theory as evidenced by the relative insensitivity of the SU-COSCC state energies with respect to the choice of orbitals than our present theory. However our formulation is more easily extendable to higher valence sectors unlike the SU-COSCC formalism. EOMCC, as expected, is the most sensitive.

3.4.2 Core Electron Ionization and Excitation

In this subsection, we will present results for core ionized states of H_2O, CH_4, HF, NH_3 and CO with suitable comparisons with COS-CC, SAC-CI and EOM-CC and core excited states of H_2O, N_2 and CH_4 with comparisons with spinorbital based Mk-MRCCSD, BW-MRCCSD and EOM-CC. We have presented a comparative study of three closely allied methods developed by us: (a) A straightforward use of the UGA-SUMRCC method with the SD truncation to describe the core-ionized/core-excited states with the ground state energy-computed by the usual single reference (SR) CCSD subtracted to generate the corresponding energy differences. The model space is comprised of certain h-p excited CSFs involving the core and some low-lying virtual orbitals as active orbitals; (b) Using the UGA-QFMRCC where the ground state cluster amplitudes feature in the computation of the ionized/excited stae allowing us to evaluate the core-IP/core-EEs directly. (c) Using a model space containing ϕ_0 and the h-p excited CSFs involving the core orbitals as the hole we may generate excitation energies directly by dropping the vacuum energy $\langle\phi_0|\overbracket{He^T}|\phi_0\rangle$ completely from the diagonal elements of the matrix of the effective Hamiltonian.The three approaches have been denoted respectively as: UGA-SUMRCC, UGA-QFMRCC and UGA-IIMS-SUMRCC in Tables 3.2-3.7. The excitation energies calculated by Kowalski et al. [52] using Mk-MRCCSD and BW-MRCCSD consider a multi-reference description of both the excited and ground state using different CASs and hence are not, in a strict sense, comparable to ours. Hartree-Fock orbitals of the ground state are used in all cases so that the phenomenon of orbital relaxation may be amply demonstrated. The spin adaptation of the wave function in our theories also modifies the computed excitation energies but due to the interplay of several factors at the same time, the role of spin adaptation itself is not immediately apparent. A study of properties sensitive to the spin of the wave function may be expected to demonstrate this aspect more conclusively.

Core electron phenomena are accompanied by strong orbital relaxation and correlation changes. This may, in principle, be taken care of by Thouless-effects in coupled-cluster theories. As explained in Section 3.2, theoretically speaking, our theories account for more relaxation than EOM-CC and our results should reflect this fact. Moreover, spinorbital based Mk-MRCCSD and BW-MRCCSD contain a complete clustering of single excitation inducing operators and therefore incorporate as much Thouless relaxation as feasible under a CCSD scheme. The closeness of our core excitation energies with Mk-MRCCSD and BW-MRCCSD to within a few tenths of an eV is an indicator of this. The spin contamination of the wave function in Mk-MRCCSD and BW-MRCCSD is another matter unrelated to the relaxation of orbitals and we do not discuss this here. They will have spin contamination only for core IPs and not for core EEs (singlet). The SAC-CI (R) results presented here use up to triple excitation operators and are hence not suitable for theoretical comparison. However, the fact that our numbers using SD truncation for core ionized states are very similar to SAC-CI (R) with three-body operators and also approaches high accuracy experimental results is a clear sign of incorporating appropriate physics at low truncation in UGA-SUMRCC and UGA-QFMRCC theories indicating how important physics can be captured at the SD truncation level, which will require higher body operatorss when Thouless-like parametrization is not used. The comparisons with EOM-CC are somewhat erratic as EOM-CC itself gives erratic levels of accuracy with change in basis and across different molecules. EOMCC does remarkably well in certain cases and fails entirely in others. Our studies indicate that for core excitations, all three variants of our theory perform consistently better than EOM-CC in different bases and for different states presumably due to better mechanism for relaxation of orbitals and correlation. However, for diabatic core ionization energies of CH_4 and NH_3, EOM-CC outperforms our theories and SAC-CI (R). It must be noted that our benchmark numbers are experimental and meaningful comparison would necessitate much more involved study using the same basis in the full CI limit to have the proper comparison. This has not been undertaken at this preliminary stage of development of our theories. In view of this, the quality of the EOM-CC numbers for CH_4 and NH_3 may just as well be due to a cancellation of errors as it might be an indication that relaxation through higher powers of one body excitations is insignificant for these molecules. The latter reason seems unlikely, as in that case, theories with better mechanism for Thouless-relaxation, viz. our UGA theories and SAC-CI (R) would have yielded equally accurate results. The ionization energies computed using our UGA-SUMRCC closely mirror COS-CC to within a few tenths of an eV indicating how closely we approach the effect of full exponentiation in a JM-like COS-CC Ansätz.

Secondly, the choice of basis should be such as to provide the function space for accurate description of core ionized and core excited states. Core ionized states only require the addition of core correlation functions such that the loss in correlation may be adequately modeled. Core excited states present a much bigger challenge since core electrons are often excited to loosely bound Rydberg states which are not well-described by standard bases. Thus, experimental excitation energies are difficult to reproduce and interpretation of core excitation spectra remain challenging. We present high accuracy experimental data for both core ionization and excitation and observe that while core ionization energies are closely reproduced and improve systematically with improvement in bases, experimental and computed core excitation energies vary significantly. More detailed studies using Rydberg orbitals and special manipulation of contraction co-efficients of the Gaussian basis have succeeded to approach the experimental values. In this paper, we present preliminary applications of our newly developed theoretical formulations and thus, such details have not been considered. However, care has been taken to clarify the extent of comparison with other theories.

Thirdly, geometry considerations are crucial, depending on the nature of the experiment we wish to compare with. We specifically mention in each case if the energy computed is diabatic (different geometries for ground and excited/ionized state taken from experiment or as used in the computations presented for comparison) or adiabatic (excitation/ionization at ground state experimental geometry). Where spectral data has been analyzed, the (0,0) vibrational band is considered for comparison with our computed energies. The geometries considered are mentioned as footnotes to the respective tables. Vibrational corrections have not been undertaken. All integrals were obtained from GAMESS-US [53]

There is a close correspondence between the IP/EE values for the example molecules

Table 3.2: **Adiabatic Core Ionization Energies for H_2O**

Basis	Ionization	ΔUGA-SUMRCC	QF-Type COSCC [4]	ΔCOSCC [4]	EOM-CCSD [55]	Expt. [54]
cc-pVDZ	O $1s^{-}1$	541.97	542.29	542.11	543.27	539.78
cc-pVTZ	O $1s^{-}1$	539.02	539.36	539.14	540.66	
cc-pcVTZ	O $1s^{-}1$	539.24	539.55	539.34	541.06	

Geometry: R (O-H) = 0.9772 Å Θ (H-O-H) = 104.52
Energies are in eV

Table 3.3: **Diabatic Core Ionization Energies for CH_4, HF and NH_3**

Molecule	Basis	Ionization	ΔUGA-SUMRCC	SAC-CI (R) [56]	EOM-CCSD [55]	Expt. [56]
CH_4	cc-pcVTZ	C $1s^{-}1$	290.50	290.50	290.83	290.86
HF	cc-pcVTZ	F $1s^{-}1$	693.40	693.89	695.42	693.80
NH_3	cc-pcVTZ	N $1s^{-}1$	405.22	405.15	405.71	405.52

Geometries for G.S.:
R (C-H) = 1.087Å, Θ (H-C-H) = 104.3; R (H-F) = 0.917Å ; R (N-H) = 1.014Å, Θ (H-N-H) = 107.2
Geometries for Ionized State:
R (C-H) = 1.039Å, Θ (H-C-H) = 104.3; R (H-F) = 0.995Å ; R (N-H) = 0.981Å, Θ (H-N-H) = 113.6Å
Energies are in eV

Table 3.4: **Adiabatic Core Ionization Energies for CO**

Basis	Ionization	ΔUGA-SUMRCC	ΔCOSCC	SAC-CI (R) [56]	EOM-CCSD [55]	Expt. [57]
cc-pVTZ	C $1s^{-}1$	295.25	295.28	296.13	297.02	296.2
cc-pcVTZ	C $1s^{-}1$	295.67	295.71	-	297.55	

Geometry: R (C-O) = 1.1283Å
Energies are in eV

studied by us as computed by the three theories, indicating that the essential physics incorporated by these theories are more or less similar. We ascribe such closeness of the results to the full exponential structure of all operators of T_μ/S_μ where valence destruction is not involved. Such is not the case for the VUMRCC approach. In fact, even for the core-ionization in the VUMRCC, the effective wave operator for a ϕ_μ is just $e^T\{1+S_\mu\}$ whereas for most of the components of S_μ the effective wave operator for the UGA-QFMRCC is e^{T+S_μ} with a full exponential structure. Thus, it does not really matter much whether a separation of the ground state cluster operator is made as above or one simply uses $T_\mu = T + S_\mu$ as the variable.

Table 3.5: **Adiabatic Core Excitation Energies for H_2O**

Basis	Excitation	ΔUGA-SUMRCC	ΔUGA - IIMS-SUMRCC	UGA-QFMRCC	EOM-CCSD [55]	Mk-MRCCSD [52]	BW-MRCCSD [52]	Expt. [52]
cc-pVDZ	$1a_1 \rightarrow 4a_1$	537.43	537.70	537.50	538.40	537.62	537.56	534.0
	$1a_1 \rightarrow 2b_1$	539.33	539.33	539.42	540.21	539.55	539.49	535.9
cc-pcVDZ	$1a_1 \rightarrow 4a_1$	536.58	536.86	536.66	537.65	-	-	
	$1a_1 \rightarrow 2b_1$	538.50	538.50	538.58	539.44	-	-	
aug-cc-pcVDZ	$1a_1 \rightarrow 4a_1$	536.24	536.61	536.24	537.55	-	-	
	$1a_1 \rightarrow 2b_1$	538.05	538.05	538.05	539.35	-	-	
cc-pVTZ	$1a_1 \rightarrow 4a_1$	534.15	534.40	534.15	535.34	534.30	534.26	
	$1a_1 \rightarrow 2b_1$	536.05	536.05	536.05	537.13	536.20	536.15	
Sadlej-pVTZ	$1a_1 \rightarrow 4a_1$	536.50	536.85	536.50	537.92	536.56	536.47	
	$1a_1 \rightarrow 2b_1$	538.27	538.27	538.27	539.60	538.34	538.35	

Geometry: R (O-H) = 0.9772 $\AA$ Θ H-O-H = 104.52
Energies are in eV

Table 3.6: **Adiabatic Core Excitation Energies for N_2**

Basis	Excitation	Δ UGA-SUMRCC	UGA-QFMRCC	EOM-CCSD [55]	Mk-MRCCSD [52]	BW-MRCCSD [52]	Expt. [52]
6-311G**	$1\Sigma_u \rightarrow 1\Pi_g$	402.53	402.48	402.20	402.37	402.52	401.2
	$1\Sigma_g \rightarrow 1\Pi_g$	402.58	402.53	402.26	402.42	402.57	400.0
cc-pVDZ	$1\Sigma_u \rightarrow 1\Pi_g$	407.67	404.75	404.38	-	-	(1.8-2 eV
	$1\Sigma_g \rightarrow 1\Pi_g$	404.83	404.80	404.43	-	-	resolution)
cc-pVTZ	$1\Sigma_u \rightarrow 1\Pi_g$	401.82	401.79	401.62	401.81	401.66	
	$1\Sigma_g \rightarrow 1\Pi_g$	401.88	401.84	401.68	401.86	401.72	
Sadlej-pVTZ	$1\Sigma_u \rightarrow 1\Pi_g$	404.66	404.63	404.05	-	-	
	$1\Sigma_g \rightarrow 1\Pi_g$	404.73	404.68	xxx	-	-	

Geometry: R (N-N) = 2.068 a. u.
Energies are in eV
xxx: Did not converge

Table 3.7: **Diabatic Core Excitation Energies for CH_4**

Basis	Excitation	ΔUGA-SUMRCC	SAC-CI (R) [56]	Expt. [56]
cc-pCVTZ	C 1s → LUMO(A_1)	287.80	288.50	287.99

Geometry of G.S.: R (C-H) = 1.087$\AA$
Geometry of Excited State.: R (C-H) = 1.032 $\AA$
Energies are in eV

3.4.3 Scalar Relativistic Effects on Core Electron Ionization

In the next subsection, the effect of scalar relativistic effects using the spin-free Dirac-Hartree-Fock Hamiltonian is studied on the molecules: H_2O, H_2S, H_2Se, NH_3 and PH_3. In all cases we have presented the relevant experimental values and the computations have been performed at the experimental geometries which are tabulated in Table 3.9. In the subsequent molecules in the two series the spin-orbit effects grow in magnitude and we cannot expect to treat it with equal facility in our current framework. We have selected large basis sets with core correlation functions in order to provide a good description of the core relaxation effects. For the relativistic computations we have used uncontracted basis sets or the dyall.cv3z basis of the DIRAC program package [58] as is the convention but for the non-relativistic computations we continue to use the corresponding contracted basis sets.

The numbers indicate two obvious trends: first, the IPs including scalar relativistic effects are closer to the experimental values and as we go down the group in the series selected by us, the contribution of the relativistic effect increases. What is somewhat surprising is that even the 1s electron of a molecule as light as water shows significant relativistic effect of the order of tenths of an eV.

Table 3.8: **Ionization energies of the 1s electron**

Molecule	Basis	NR Orbitals	4c-DHF Orbitals	Experiment
H_2O	cc-pCVTZ	539.38	539.84	539.78^a
	cc-pCVQZ	539.33	539.74	
H_2S	cc-pCVDZ	2473.90	2482.42	2478.91^b
	cc-pCVDZ (u)	2475.78	2486.49	2478.32^c
	cc-pCVTZ	2471.57	2479.86	
	cc-pCVTZ (u)	2472.24	2480.64	
H_2Se	dyall.c3v	-	12692.29	12657.8±0.7^d
NH_3	dyall.cv3z	-	405.5735543	405.6^e
	cc-pCVTZ	405.2212503	-	
PH_3	dyall.cv3z	-	2153.715676	2150.88^f
	cc-pCVTZ	2146.869621	-	2150.5^g

Atomic core ionization value
All values are in eV
Ref. a[59]; Ref. b[60]; Ref. c[61]; Ref. d[62]; Ref. e[63]; Ref. f[64]; Ref. g[63]

Table 3.9: **Geometries of molecules with heavy atom, A**

	A-H	H-A-H
H_2O	0.9772 au	104.52
H_2S	2.5251 au	92.06
H_2Se	1.4567 Å	91
NH_3	1.3366 Å	92.06
PH_3	2.674 au	93.3

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Chapter 4

Behavior of Molecules under External Perturbation

4.1 Introduction

The interaction of molecules with electric and magnetic fields lies at the heart of interpreting their behavior under external perturbation such as irradiation by electromagnetic radiation. For ab initio quantum mechanical methods, two approaches are available for computation of molecular properties: numerical differentiation using the finite field technique and the method of analytic gradients. Several extensive reviews are available [1, 2, 3] and we do not go into a detailed discussion of all the techniques. A brief background is provided in the paragraphs below to elucidate better our developments in the sections to follow.

A perturbative expansion, as shown in Eq, 4.1, of the energy of a molecular state yields the molecular properties as the coefficients accompanying each term of the expansion in the field, X.

$$E(X) = E^{(0)} + E^{(1)}X + \frac{1}{2}E^{(2)}X^2 + ... \tag{4.1}$$

The molecular property is associated with the coefficients of X at each order of perturbation. For static perturbations such as constant electric and magnetic fields or nuclear geometries, the coefficients can be shown to be related to the derivatives of the energy through a Taylor expansion of the energy about the zero-field situation as shown in Eq. 4.2.

$$E(X) = E^{(0)} + \frac{\partial E}{\partial X}\Big|_{X=0} X + \frac{1}{2}\frac{\partial^2 E}{\partial X^2}\Big|_{X=0} X^2 + ... \tag{4.2}$$

and yield time independent properties. For example, for electric properties, the definitions of permanent dipole moment μ and polarizability α are related to the derivatives of the energy with respect to the electric field, ε, as follows:

$$\begin{aligned} \mu &= -\frac{\partial E}{\partial \varepsilon}\Big|_{\varepsilon=0} && (4.3) \\ \alpha &= -\frac{1}{2}\frac{\partial^2 E}{\partial \varepsilon^2}\Big|_{\varepsilon=0} && (4.4) \end{aligned}$$

The electronic Hamiltonian for a molecular system perturbed by an external field is a function of two sets of distinct parameters: external parameters, X, such as electric/magnetic field or the geometry by virtue of the BO approximation and internal wave-function parameters, λ, which include the MO coefficients and the parameters of the wave operator, for example the cluster amplitudes of CC or the coefficients of CI. The wave-function parameters, λ, also have an implicit dependence on X which may be denoted by $\lambda(X)$. Considering that the wave-function parameters have been predetermined as λ_x by some method for a given value of X, the total derivative of E can be denoted as:

$$\frac{\delta E(X,\lambda(X))}{\delta X} = E(0,\lambda_x) + \frac{\partial E(X,\lambda)}{\partial \lambda}\Big|_{\lambda=\lambda_x} \frac{\partial \lambda}{\partial X}\Big|_{\lambda=\lambda_x} \tag{4.5}$$

For a variational wave-function optimized for every X, $\frac{\partial E}{\partial \lambda} = 0$ for all values of X. Thus, the total derivative and partial derivative become identical and the wave-function response, $\frac{\partial \lambda}{\partial X}$ is not needed for computing the properties at first order. This is in accordance with the familiar 2n+1 rule of perturbation theory. Of course, one must ensure that one is dealing with the response of the parameters with respect to which the wave-function has been made stationary. For example, the CI wave-function is stationary with respect to the CI coefficients but not the orbital rotation parameters which have been optimized at the SCF level. Thus, for us to consider the CI wave-function as variational, the orbitals will also have to be optimized in the presence of the perturbation and correlation. We would thus end-up with a large-scale CAS-SCF wave-function which is of course fully variational. CC theories are also non-variational and special techniques have been developed to make them conform to the variational conditions which we shall discuss in a moment.

Since the energy of the molecule can be expressed as an expectation value of the Hamiltonian of the system:

$$E(X) = \langle\Psi| H(X) |\Psi\rangle \tag{4.6}$$

some further simplifications for obtaining the derivatives of the energy with respect to X may be engineered. For exact wave-functions, the Hellmann-Feynmann theorem states that:

$$\frac{\delta E(X)}{\delta X} = \langle\Psi| \frac{\delta H(X)}{\delta X} |\Psi\rangle \,. \tag{4.7}$$

Unfortunately, the wave-functions we deal with in this thesis are of the coupled cluster form. In addition to being non-variational, they are neither exact nor are the left and right eigenvectors of the Schrödinger Hamiltonian adjoints of each other. It was then envisaged that instead of an expectation value, if one represented the energy as the projection of the Schrödinger equation for the approximate wave-function by a suitable bra function, one may not only calculate the derivatives of the energy as a matrix element of the derivatives of the Hamiltonian but also restore the familiar 2n+1 rule of variational wave-functions to non-variational wave-functions. This was called the method of the Quasi-Energy Lagrangian and is a very powerful technique for formulating and computing properties from arbitrary wave-functions. The energy from any non-variational wave-function may be made stationary with respect to a set of suitably chosen Lagrange's multipliers, say, λ. It can be shown that the λs so determined actually obey a more stringent 2n+2 rule further enhancing the efficacy and beauty of the Lagrangian formulation of analytic gradients, as it is commonly called.

For an arbitrary non-variational wave-function, ψ, parametrized by some set of variables, $\{t_i\}$, let us denote the working equations for t_i as:

$$R_i(t) = 0 \tag{4.8}$$

and the energy as E(t). The Lagrangian, $\mathcal{L}$, may be constructed to give back the energy of the system when the t_is have their optimized values by using Eq. 4.8 as a constraint with corresponding Lagrange's undetermined multipliers, λ_i. Additional constraints may also be imposed as required.

$$\mathcal{L} = E(t) + \sum_j \lambda_j R_j(t) \tag{4.9}$$

The equations for obtaining t_i are obtained by making the $\mathcal{L}$ stationary with respect to λ_i and the equations for obtaining λ_i are obtained by making the $\mathcal{L}$ stationary with respect to t_i. The λ_is thus satisfy the equation:

$$\frac{\delta E(t)}{\delta t_i} + \sum_j \lambda_j \frac{\delta R_j(t)}{\delta t_i} = 0 \tag{4.10}$$

and Eq. 4.8 becomes the stationarity condition for λ_i. Since the functional $\mathcal{L}$ in Eq. 4.8 is sought to be made stationary with respect to both $\{\lambda_i\}$ and $\{t_i\}$, so as to yield the desired energy at the stationary point, we may call this strategy as using a *bivariational* principle. It is interesting to note that the Lagrangian approach gives the Hylleraas functional when applied to a perturbation expression and may also be generalized to time-dependent properties.

This bivariational approach is particularly useful for coupled cluster theories where the Lagrange's multipliers may be identified as the amplitudes of the cluster operator Ansatz for the bra function taken as:

$$\langle\psi| = \langle\phi|\,(1+\Lambda)e^{-T} \tag{4.11}$$

where Λ is a de-excitation operator having amplitude, λ and the Ts are the usual excitation operators, ϕ being the HF function. The Lagrangian for the single reference coupled cluster theory is thus simply:

$$\begin{aligned} \mathcal{L} &= \langle\phi|\,(1+\Lambda)e^{-T}He^{T}\,|\phi\rangle && (4.12) \\ &= E_{CC} + \sum_l \langle\phi|\,\Lambda_l(e^{-T}He^{T})_l\,|\phi\rangle && (4.13) \end{aligned}$$

where ‘l’ is an excited function index. A perturbative expansion of the Lagrangian allows us to determine the expressions for the molecular properties at each order.

In this chapter we present the analytic gradient formulation of the single CSF limit of UGA-SUMRCC which has been described in Chaps. 2 and 3. We call this theory UGA-OSCC. We also use the finite field technique to compute properties of some small molecules under a static electric field viz. dipole moment and polarizability. The strength of this theory lies in that it can address non-singlet molecular states at the coupled-cluster level providing a spin-adapted starting function for computing properties related to external perturbations. A correct description of the zeroth order function is expected to translate into a higher accuracy for computed properties even if the perturbation breaks the spin-scalar nature of the Hamiltonian. The UGA-OSCC theory uses a normal ordered exponential ansatz where the cluster operators are unitary group generators and the normal ordering is with respect to a suitable closed shell vacuum designed to ensure commuting T-operators even when they involve destruction of partially occupied orbitals. The working equations for this formulation are projection equations with the occurrence of quasi-diagonal reduced density matrices (RDM) of the model functions. This difference adds to the complexity of the gradient formulation making it more than a routine exercise. Operators of the left eigenvector, $1 + \Lambda$, of the Schrödinger equation, already occurs in the projection equations for the T-amplitudes. Since certain truncations are operationally imposed, the terms in the equations for Λ and subsequently the perturbed OSCC densities must be compatible. Moreover, the ranks of the RDMs involved increases with increase in the number of active electrons and some reasonable truncations must be effected to make the theory implementationally viable.

4.2 *The Lagrangian*

The working equations for the cluster amplitudes in UGA-OSCC are as follows:

$$\langle\chi_\mu^l|\{\overline{H}_\mu\}|\phi_\mu\rangle - \langle\chi_\mu^l|\{\overbracket{e^{T_\mu}W_{\mu\mu}}\}|\phi_\mu\rangle \;=\; 0 \tag{4.14}$$

$$\sum_n \langle\chi_\mu^l|\{G_\mu\}|\phi_\mu\rangle = 0 \tag{4.15}$$

and,

$$\overline{H}_\mu = \overbracket{He^{T_\mu}} \tag{4.16}$$

$$W_{\mu\mu} = [\overline{H}_\mu]_{\mu\mu} \tag{4.17}$$

$$G_\mu = \overline{H}_\mu - \overbracket{e^{T_\mu}W_{\mu\mu}}, \tag{4.18}$$

The energy expression is given by:

$$\varepsilon_\mu = (H_{eff})_{\mu\mu} = \langle\phi_\mu|\{\overline{H}_\mu\}|\phi_\mu\rangle = E_{core} + \langle\phi_\mu|\{W_{\mu\mu}\}|\phi_\mu\rangle \tag{4.19}$$

The index μ is carried to keep in mind that ϕ_μ is an open-shell configuration state function (CSF) and the normal ordering denoted by $\{...\}$, for the T_μs is with respect to the largest common closed shell part of the ϕ_μs. ε_μ, thus, not only involves the 0-body part of $\overline{H}_\mu$ but also the $\overline{H}^{1b}_{\mu\ cl}$, $\overline{H}^{2b}_{\mu\ cl}$, ..., $\overline{H}^{nb}_{\mu\ cl}$ depending upon the number of active orbitals, n_a, in ϕ_μ. For a single CSF, these active orbitals can be chosen to be only the singly occupied ones by suitable choice of vacuum for normal ordering.

A Lagrangian which faithfully represents Eqns. (4.14) and (4.19) can be constructed as follows.

$$\begin{aligned}\mathcal{L}_\mu &= \varepsilon_\mu + \sum_m \langle\chi^m_\mu|\{\overline{H}_\mu\}|\phi_\mu\rangle - \sum_m \langle\chi^m_\mu|\{\wick{\c{e}^{T_\mu}\c{W}_{\mu\mu}}\}|\phi_\mu\rangle \\ &= \underbrace{\langle\phi_\mu|\{\overline{H}_\mu\}|\phi_\mu\rangle}_{1} + \underbrace{\sum_m \langle\phi_\mu|\Lambda^\mu_m[\{\overline{H}_\mu\}]^m_\mu|\phi_\mu\rangle}_{2} - \underbrace{\sum_m \langle\phi_\mu|\Lambda^\mu_m[\{\wick{\c{e}^{T_\mu}\c{W}_{\mu\mu}}\}]^m_\mu|\phi_\mu\rangle}_{3}\end{aligned} \tag{4.20}$$

The $\Lambda^\mu_l = \lambda^\mu_l E^\mu_l$ are de-excitation operators whose amplitudes, λ^μ_l, may be identified with the Lagrangian multipliers for the equations defining the cluster amplitudes, $T^l_\mu = t^l_\mu E^l_\mu$. In a simplified form, we can write the Lagrangian as:

$$\mathcal{L}_\mu = \langle\phi_\mu|(1+\Lambda_\mu)\{G_\mu\}|\phi_\mu\rangle \tag{4.21}$$

4.3 The Equations Determining the Set $\{\lambda^\mu_l\}$

As customary, the equations determining, λ^μ_l, may be obtained by differentiating $\mathcal{L}_\mu$ with t^l_μ. The differentiation of the Terms 1 and 2 are similar to that for single reference coupled cluster (SRCC) theory. Term 3 is very different in that the t^l_μs occur in two places namely contracted to $W_{\mu\mu}$ and within $W_{\mu\mu}$. The differentiation of Term 3 will thus result in two terms, which we call Terms 3A and 3B respectively.

$$\mathit{Term\ 3A} = \sum_m \langle\phi_\mu|\Lambda^\mu_m[\{\wick{\c1{E}^l_\mu\c2{e}^{T_\mu}\c2{\c1{W}}_{\mu\mu}}\}]^m_\mu|\phi_\mu\rangle \tag{4.22}$$

$$\mathit{Term\ 3B} = \sum_m \langle\phi_\mu|\Lambda^\mu_m[\{\wick{\c1{e}^{T_\mu}[\c3{\c2{H}}\c2{\c1{e}}^{T_\mu}\c3{E}^l_\mu]_{\mu\mu}}\}]^m_\mu|\phi_\mu\rangle \tag{4.23}$$

Before we embark on the explicit terms to be computed, we note the major differences of this gradient formulation with other coupled cluster gradient formulations be it single reference or multi-reference. The most significant difference is that the equations for the T-amplitudes are not amplitude equations but projection equations. Thus, G_μs of several ranks, n, (see Eq. (4.15)) contribute to an equation for a cluster amplitude and not all of them correspond to a t-amplitude. Thus, on convergence of the T equations, linear combinations of the G_μs and not individual G_μs are zero. Moreover, the projection equations involve matrix elements between CSFs and not determinants. Thus, the Lagrangian for UGA-OSCC involves reduced density matrices (RDM), $\Gamma_{\mu\mu}$, in addition to H, T_μ and Λ_μ. This implies that with an increase in the number of active orbitals, the possible ranks of the RDMs, the G_μs and hence, number of possible terms in the Lagrangian would keep on increasing. For practical purposes, some truncation of the ranks of the RDMs to be used must be employed and we must be careful to maintain a correspondence between the terms included in the T equations, those in the Λ equations and subsequently, those in the $\overbracket{\Lambda_\mu e^{T_\mu}}$ composites (ie. the so-called CC perturbed densities) in view of the truncation. While determining the terms contributing to the equations for λ, all possible de-excitation looking terms arising from the differentiated terms of the $\mathcal{L}$ (removing the operator of T^l_μ, ie. E^l_μ as well) are constructed and then a re-projection by E^l_μ from the right is carried out. We treat the differentiation of the $\overbracket{e^{T_\mu}W_{\mu\mu}}$ term differently from the $\overbracket{He^{T_\mu}}$ term. Since we have gone quite some distance towards the numerical implementation of the analytic gradient method for the UGA-based MRCCs, we have discussed the technical details of this procedure separately in Sec. 5.2.8 of Chap. 5. Since there are no numbers yet from the code, we are presenting results using numerical gradients in Sec. 4.4 of this chapter.

4.4 Numerical Gradients of UGA-OSCC

To indicate the expected accuracy of our gradient formulation we present here the electric properties of some open-shell molecules calculated by means of the technique of numerical gradients. We have used five-point numerical gradients using electric fields 0.000, ±0.001 and ±0.002. We have corroborated the results by fitting a fourth degree polynomial to the data as well. We find that while dipole moments computed using fields of 0.0000, ±0.0001 and ±0.0002 and 0.000, ±0.001 and ±0.002 agree upto $10^{-3}au$, the polarizabilities are much better reproduced with the latter range of fields. We have thus chosen this range of electric fields for our computations. The electric field has been applied along the z-axis which is selected as the bonding axis for CN, CH and SiH radicals such that the cylindrical symmetry of these linear molecules is not broken. For NO field along x, y and z-axes have been employed to determine the diagonal elements of the polarizability tensor for NO and thereby obtain the average value. Fields in the x and y directions break the symmetry of the molecule and result in a mixing of the model functions which are otherwise orthogonal by symmetry. The degeneracy of the π orbitals is also broken by the electric field. The results indicate that our theory closely mirrors the accuracy of UGA-CCSD of Li and Paldus [4].

Table 4.1: **Dipole moment and polarizability of the CN radical in various basis sets computed using numerical gradients of UGA-OSCC**

Basis	μ [u]	μ [r]	α_{zz} [u]	α_{zz} [r]
cc-pVDZ	0.542	0.547	26.57	26.7475
aug-cc-PVTZ	0.611	0.606	27.86	28.3712
Sadlej	0.613	0.613	30.48	30.4819
ANO	0.611	0.610	34.34	35.0662
Expt	0.57			

Geometry: C-N = 2.21512 au

Table 4.2: **Dipole moments of CH, SiH and NO using Sadlej-pVTZ basis**

μ	$CH(^2\Pi)$	$SiH(^2\Pi)$	$NO(^2\Pi)$	$NO(^2\Sigma)$
UGA-OSCC [u]	0.537	0.039	0.060	0.702
UGA-OSCC [r]	0.538	0.049	-0.056	0.696
CVA-FS-MRCCSD [5]	0.543	0.063	-0.073	0.674
FS-MRCCSD (ff) [5]	0.520	0.046	-0.041	0.698
UGA-CCSD [6]	0.535	0.037		
Expt.	0.574 [7]	0.023		

Geometry: C-H = 2.11648 au; Si-H = 2.84 au; N-O = 2.17464 au

Table 4.3: **Polarizabilities of CH, SiH and NO using Sadlej-pVTZ basis**

α_{zz}	$CH(^2\Pi)$	$SiH(^2\Pi)$	$NO(^2\Pi)$	$NO(^2\Sigma)$
UGA-OSCC [u]	16.56	37.22	14.50	244.20
UGA-OSCC [r]	16.64	38.44	15.33	241.20
CVA-FS-MRCCSD [5]	15.86	37.44	14.72	243.99
FS-MRCCSD (ff) [5]	16.20	38.30		240.90
UGA-CCSD [6]	16.22	38.81		

Geometry: C-H = 2.11648 au; Si-H = 2.84 au; N-O = 2.17464 au

Table 4.4: **Diagonal elements of the polarizability tensor of the NO radical computed in the Sadlej-pVTZ basis**

	α_{zz}	α_{xx}	α_{yy}	$\langle\alpha\rangle$
UGA-OSCC	15.33	9.21	10.10	11.55
ROHF-CCSD (ff)	15.29	9.1	10.08	11.49
ROHF-CCSD(T) (ff)	15.34	9.22	10.21	11.59
CVA-FSMRCCSD [5]	14.72	8.9	9.96	11.19
Refractivity Measurement	15.24	9.67	9.67	11.53
Expt [8, 9]				11.5180.013

Geometry: N-O = 2.17464 au

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Chapter 5

Algorithm and Programmatic Organization

5.1 The Set of MRCC Programs

The two theories discussed in Chapter 2, the UGA-SUMRCC and UGA-QFMRCC, are integrated in the MRCC program package developed as a part of this thesis project. The package also has the potential for UGA-SSMRCC runs. The code is designed to handle any user-specified model space whether complete or incomplete. The code takes as input one and two-body Hamiltonian integrals in molecular orbital (MO) basis. For this, the code is interfaced to GAMESS-US, DIRAC and LONDON. The complete model space one-particle RDMs are always obtained non-interactively from the GUGA module of GAMESS-US through a simple file I/O. The MRCC program package can of course also run SRCC computations for which gradient modules are also available for computation of up to second order properties but not molecular geometry optimizations yet. The gradient section of the code for open-shells is not fully functional yet and we only discuss matters of principle in this regard.

In Sec. 5.2 we discuss how the non-trivial parts of the programs have been handled and in Sec. 5.3, we give a brief idea of the computational cost and scaling of our theories.

5.2 Computational Organization

The codes take inputs from two files called *mrcc.inp* and *modelfn.inp*. The first file contains basic information such as number of basis functions, number of inactive and active orbitals, number of model functions, etc. and control information such as which theory to run, to compute properties or not, convergence thresholds, printing thresholds, etc. The second file contains the user-defined list of model functions (CSF) in terms of the occupancy of the active orbitals. If two CSFs have the same occupancy but different spin-coupling schemes, they have to be repeated in the input file. The CSF occupancies are tallied with the diagonal elements of the 1p-RDMs from GUGA computations to obtain the required diagonal and transition RDMs. Full sample input files are provided in Appendix G. In addition MO integral files generated from GAMESS, DIRAC or LONDON must be supplied. MCSCF-based UGA-SSMRCC can only run in conjunction with GAMESS and the files required are somewhat different which must be correctly entered in the input files.

With this information, the code constructs the RDMs required (Sec. 5.2.1), carries out the construction of the G-blocks using an automatic sequence optimizer and tensor contraction engine for multiple tensor contractions (Sec. 5.2.2), constructs the residues for the working equations of the cluster operator (Sec. 5.2.5) and updates the manifold of cluster operators dictated by the theory (Secs. 5.2.6 and 5.2.7). The special considerations required for handling IMS and the modifications for the implementation of the UGA-QFMRCC theory have been discussed in Sec. 5.2.3 and Sec. 5.2.4 respectively.

5.2.1 Construction of IMS Density Matrices for mh-np Valence Sectors

The GUGA module of GAMESS constructs only elements of the 1p transition density matrices or RDMs, $\gamma_{\mu\nu}{}^{v}_{u}$, between two Gel'fand adapted CSFs, ϕ_μ and ϕ_ν.

$$\gamma_{\mu\nu}{}^{v}_{u} = \langle\phi_\nu|\, E^v_u \,|\phi_\mu\rangle \tag{5.1}$$

The doubly occupied core function is taken as the vacuum for this construction. However, for our purposes we may choose a larger vacuum and treat the model functions as belonging to a hole or mixed hole-particle sector. The RDMs must then be suitably modified. Specifically, the normal ordering of the generators of the unitary group, E^v_u, must be changed. For example, for our computations using the 1h-1p sector for excited states, the most natural choice of vacuum is the HF function of the ground state with N electrons. This necessitates a shift of the normal ordering of E^v_u from being with respect to the core function with N-2 electrons to the HF function with N electrons. The corresponding elements of the RDMs, $\bar{\gamma}_{\mu\nu}{}^{v}_{u}$, can be easily redefined by Eq. 5.2.

$$\bar{\gamma}_{\mu\nu}{}^{v}_{u} = \gamma_{\mu\nu}{}^{v}_{u} - \Gamma^v_u\delta_{\mu\nu} \tag{5.2}$$

where, Γ^v_u is an element of the density matrix of the vacuum and the diagonal elements have a value of 2 for occupied orbitals and 0 for unoccupied orbitals in the spin-free case. The two-body Γ for the vacuum is also constructed using Eq. 5.3, as it is required for the construction of the two-body RDMs featuring in our UGA-MRCC equations.

$$\Gamma^{pr}_{qs} = \Gamma^p_q\Gamma^r_s - \delta_{qr}\Gamma^p_s \tag{5.3}$$

The elements of the 1p RDM with our choice of vacuum in an IMS, $\tilde{\gamma}_{\mu\nu}{}^{v}_{u}$, are generated from the CSF occupancies provided in the input file, *modelfn.inp* for the 1h-1p case. Alternatively, for larger model spaces, the user-defined CSFs are identified in the list of CSFs generated by GAMESS and a subset of $\bar{\gamma}_{\mu\nu}{}^{v}_{u}$ in the CAS is defined as $\tilde{\gamma}_{\mu\nu}{}^{v}_{u}$ in the IMS. The construction of the elements of the two-body RDMs in the IMS involves the use of an identity projector and hence requires both $\bar{\gamma}_{\mu\nu}{}^{v}_{u}$ and $\tilde{\gamma}_{\mu\nu}{}^{v}_{u}$ (Eq. 5.4).

$$\tilde{\Gamma}_{\mu\nu}{}^{pr}_{qs} = -(\delta_{rq} - \frac{1}{2}\Gamma^r_q)\tilde{\gamma}_{\mu\nu}{}^{p}_{s} + \frac{1}{2}\Gamma^p_s\tilde{\gamma}_{\mu\nu}{}^{r}_{q} - ((\delta_{rq} - \frac{1}{2}\Gamma^r_q)\Gamma^p_s + \Gamma^{pr}_{qs} - \Gamma^p_q\Gamma^r_s + \frac{1}{2}\Gamma^p_s\Gamma^r_q)\delta_{\mu\nu} + \sum_{\lambda} \bar{\gamma}_{\mu\lambda}{}^{p}_{q}\bar{\gamma}_{\lambda\nu}{}^{r}_{s} \tag{5.4}$$

The $\tilde{\gamma}$ and $\tilde{\Gamma}$ matrices are finally used in our projection equations and H_{eff} matrix. By suitably defining the vacuum density Γ, we can in principle use any choice of vacuum in our code.

5.2.2 Automatic Sequence Optimizer and Tensor Contraction Engine for Multiple Tensor Contractions

The expressions for the construction of the direct term in the G-blocks have been obtained using an Automatic Expression Generator (AEG) written in Python [1]. A Tensor Contraction Engine (TCE) has been developed by us in collaboration with Dr. Simen Reine, CTCC, Oslo, the details of which will appear in a forthcoming publication along with timing studies but we delineate the salient principles here for completeness. An automatic code generator (ACG) [1] acts as a translator between the AEG and the TCE.

Our MRCC codes are coded for LCCSD, CCD and CCSD runs. The last two options involve a sequence of contractions involving up to five tensors of varying dimensions to be contracted. The TCE determines the sequence in which the tensors are to be contracted for optimal utilization of floating point operations (FLOPs) and memory resources. The TCE counts the number of FLOPs required for all the possible sequences of contractions and chooses the best path. This criteria encompasses both operation and memory considerations. Since, this determination is carried out at run-time, this TCE is also capable of taking into consideration the differences in the optimal sequence for different basis set sizes and number of inactive hole, active and inactive virtual orbitals. Once the sequence is selected, the tensors are suitably permuted to make them amenable to contraction by the DGEMM routines from the LAPACK library. Care is taken to optimally carry out the permutations which are likely to become bottlenecks in the code if done wrong. The routines have been designed to allow external specification of the orbital ranges of the output array. This is specially relevant for optimal memory usage in our case as three and higher body G-blocks feature in our projection equations but not all at once. We might mention that the largest dimension of the three-body G-blocks, for instance, is $n_{act}^2 n_h^2 n_p^2$ where n_{act} is the number of active orbitals, n_h is the number of inactive holes and n_p is the number of inactive particle orbitals.

5.2.3 Handling H_{eff} and $W_{\nu\mu}$ for IMS

To incorporate the lack of IN of Ω_μ in the definition of H_{eff}, we proceed as mentioned in Eq. 2.53 at each step of iteration. Using the expression for G_μ in Eq. 2.26, at any iterative step (i+1) we can write:

$$\langle\phi_\lambda|[\{e^{T_\mu}\}\{\overline{H}^{(i)}_\mu\}]_{cl}|\phi_\mu\rangle - \langle\phi_\lambda|\sum_\nu[\{e^{T_\mu}\}\{e^{T_\nu - T_\mu}\overbracket{(e^{T_\nu} - 1)W^{(i)}_{\nu\mu}}\}]_{cl}$$
$$+[\{e^{T_\mu}\}\{(e^{T_\nu - T_\mu} - 1)W^{(i)}_{\nu\mu}\}]_{cl}|\phi_\mu\rangle = H^{(i+1)}_{eff,\lambda\mu} \tag{5.5}$$

where,

$$W^{(i)}_{\nu\mu}|\phi_\mu\rangle = |\phi_\nu\rangle\langle\phi_\nu|H^{(i)}_{eff}|\phi_\mu\rangle \tag{5.6}$$

We start the iteration of H_{eff} with the following expression:

$$H^{(0)}_{eff,\lambda\mu} = \overline{H}^{(0)}_{\lambda\mu} = H_{\lambda\mu} \tag{5.7}$$

Here an important point to notice is that, in each step of iteration, we have chosen our H_{eff} in such a manner that it corresponds to the true solution for the residue 2.28:

$$R_{cl,\lambda\mu} = 0 \tag{5.8}$$

Subsequently, we will diagonalize H_{eff} to get the energies for all the 'k' states.

To implement the sufficiency variant of the parent UGA-SUMRCC, we have separated out the blocks corresponding to linearly dependent operators. Then the residues for each of the operators are computed and the iteration is performed until the residue become zero. The algorithm for H_{eff} for the sufficiency variant is exactly the same as that for the parent UGA-SUMRCC.

5.2.4 Special Considerations for UGA-QFMRCC

For UGA-QFMRCC, we need to construct all possible $\overline{H} = \overbracket{He}^{T}$ (may be three body or higher) followed by a construction of $\overbracket{\overline{H}e}^{S_\mu}$. These connected composites comprise the G blocks which feature in the working equations determining S_μ. H_{eff} is also constructed from this composite. S_μs are the amplitudes embodying differential correlation for the CSF, ϕ_μ. Instead of a step-wise construction, which appears to be the most obvious, in our implementation our goal has been to generate all diagrams possible in $\overbracket{\overline{H}e}^{S_\mu}$ without a prior construction of all possible $\overline{H}$. We have achieved this in the following manner:

1. Carry out an SRCCSD computation and write the closed shell ground state Ts to file and also store the correlation energy, E_{corr} for each model function.
2. Read in the Ts in an array defined for the target sector, ie. in generalized hole-particle dimensions with entries in valid locations and the rest zero

3. Define a composite array called S'_μ containing $T + S_\mu$
4. Evaluate all possible $\overbracket{He}^{S'_\mu}$ composites. This involves the same set of diagrams as the $\overbracket{He}^{T_\mu}$ composites used in UGA-SUMRCC. The intermediate three and higher body $\bar{H}$s are also generated implicitly.
5. The IP-like, EA-like and EE-like portions from the G-blocks are picked up as the $W_{\nu\mu}$s and suitably multiplied with density matrices to give contributions to H_{eff}. Additionally, closed terms involving the Hamiltonian and both T and S_μs or only S_μ contribute to H_{eff}, viz.
$(\overbracket{FS}_{1\mu})$, $(\overbracket{VS}_{2\mu})$, $(\overbracket{VS}^2_{1\mu})$, $(\overbracket{\overbracket{VT}_1 S}_{1\mu})$
However, to reduce computation, we do not compute these terms individually but rather construct $(\overbracket{FS}'_{1\mu})$,$(\overbracket{VS}'_{2\mu})$, $(\overbracket{VS}'_{1\mu}{}^2)$ and then drop the E_{corr} computed in Step (1) from H_{eff} to get $\overline{H}_{eff}$ at each iteration step.
6. The algorithm for obtaining the correct $\overline{H}_{eff}$ in an IMS is exactly the same as for the parent UGA-SUMRCC.
7. Diagonalization of the final $\overline{H}_{eff}$ yields excitation energies directly.

5.2.5 Projection Equations

To construct the residuals, R^l_μ, along the lines of Eq. 2.27 we need to evaluate the projection of the operators of the cluster operators on all possible G-blocks. This amounts to evaluating a weighted sum of the amplitudes of the G-blocks, g, for each cluster operator where the weights are the elements of the RDMs for a given ϕ_μ (viz. Eq. 2.72). Since, the cluster operators are not normalized to unity, we need to carry out a normalization of R^l_μ to prevent an imbalance between the updates of the various cluster amplitudes (see Sec. 5.2.7). While this has no direct effect on the theoretical requirements and does not affect the final converged solution, it is found to play a vital role in the convergence behavior of the equations. In fact, in most cases, we were unable to obtain convergence without normalization.

The constraint of using specific combinations of T-operators (viz. Tables 2.1 and 2.2) in order to ensure a LIN excitation space is also implemented at this juncture. For linearly dependent operators the residuals are constrained to be properly signed multiples of each other such that the cluster operators behave as if they have a common amplitude associated with the proper combination of elementary operators. This is just another way of saying that we actually project with a given combination of elementary operators.

In this thesis we have handled only one and two-body RDMs in the projection equations and constructing and storing them is computationally better. However, one can imagine that the RDMs would grow in rank and size very quickly for larger active spaces, making storage a bottleneck. In that case, one can use the decomposition formula of a high rank RDM explicitly in the projection equations.

5.2.6 Discarding Gs not Corresponding to Ts

As discussed in Chaps. 2 and 3, not all of the G-blocks we construct contribute individually to cluster amplitudes. The residuals mentioned in Sec. 5.2.5 are not separate arrays but overwritten G-block arrays. This makes it necessary to remove the quantities that do not correspond to Ts although they contribute to the construction of residuals via the projection equations. This step could have been clubbed with the selective generation of residuals but we have chosen to keep this separate to avoid unnecessary occupancy-based checks in the projection equations and improve modularity.

5.2.7 Convergence Scheme

A Jacobi iteration scheme is employed to iterate the cluster amplitudes. The residuals, R^l_μ, are used to update the amplitudes of T by Eq. 5.9.

$$T^{l\,(i+1)}_\mu = T^{l\,(i)}_\mu - \frac{R^{l\,(i)}_\mu}{D^l_\mu} \tag{5.9}$$

where the exact structure of the denominator, D^l_μ, is immaterial so long as it provides a balanced updating of the cluster amplitudes. In our code we have chosen the following expressions for the denominators of the one and two-body cluster operators, T^A_I and T^{AB}_{IJ}, where I,J,etc. and A,B,etc. are generic indices for occupied and unoccupied orbitals respectively in ϕ_μ and 'u' denotes the singly occupied active orbitals:

$$\begin{aligned} D^A_I &= \varepsilon_A - \varepsilon_I - \sum_u v^{Au}_{Au} + \sum_u v^{Iu}_{Iu} && (5.10) \\ D^{AB}_{IJ} &= \varepsilon_A + \varepsilon_B - \varepsilon_I - \varepsilon_J - \sum_u v^{Au}_{Au} - \sum_u v^{Bu}_{Bu} + \sum_u v^{Iu}_{Iu} + \sum_u v^{Ju}_{Ju} && (5.11) \end{aligned}$$

The orbital energies, ε, are obtained from the HF mean-field computation for the vacuum chosen.

For accelerating the convergence of the cluster amplitudes we employ the DIIS extrapolation method. Our implementation has two possible schemes for DIIS. The first involves a user-specified fixed size of the iterative sub-space, *ndiis*, and has provision for selecting the intervals, *nskip*, at which the extrapolation will be carried out. Usually, one selects *nskip* > *ndiis* leading to non-overlapping iterative sub-spaces. The second scheme uses a cumulative iterative sub-space for iteration and the user may specify the minimum (*diismin*) and the maximum (*diismax*) number of vectors to be kept in the iterative sub-space. There is thus always an overlap between the vector spaces used for two consecutive extrapolations. Both schemes are found to perform similarly in most cases although sometimes one yields significantly improved convergence over the other. No clear trends were noted.

The convergence check has two levels: first, the average of the absolute values of the residuals for all the non-zero Ts is brought below the set threshold and then, the absolute value of any individual residuals which are still above the threshold are added to the error measure, ϵ. The cluster amplitudes are iterated till ϵ is below the user-defined threshold. In the results presented in this thesis a convergence threshold of 10^{-8} was mostly used.

5.2.8 Equations for Obtaining λ

Moving on, let us take the example of an N electron system where there is only 1 active electron and the vacuum chosen has (N-1) electrons. Thus, the target sector is a '1-particle' sector. The RDM involved is only of rank 1 and can be explicitly denoted as ${\Gamma_{\mu}}_{u}^{u}$. The G_μs are of maximum rank n=3. The index μ on W has been suppressed for simplicity while the diagonality of the RDMs has not been assumed to allow us to easily extend the implementation to higher target sectors. We denote the term obtained after differentiation of $\mathcal{L}_\mu$ with t_I^A as ${R_\mu}_A^I$ where I can be inactive hole orbitals (i,j,...) or active orbitals (u,v,w,...) and A can be inactive particle orbitals (a,b,...) or active orbitals in ϕ_μ. Primed indices, i',j',..,etc., indicate generalized holes (inactive holes+actives) and, a',b',...,etc., are generalized particles (actives+inactive particles). The terms in the differentiated $\mathcal{L}_\mu$ coming from Term 3A can be enlisted below:

$$\begin{aligned}
{R_\mu}_{a'}^{w} &\Leftarrow \lambda_{a'}^{u} E_{w}^{a'} W_{v}^{w} {\Gamma_{\mu}}_{v}^{u} \;\; \forall\, a', w \\
{R_\mu}_{a'b'}^{wj'} &\Leftarrow \lambda_{a'b'}^{uj'} E_{wj'}^{a'b'} W_{v}^{w} {\Gamma_{\mu}}_{v}^{u} \;\; \forall\, a', b', w, j' \\
{R_\mu}_{a'b'}^{wj'} &\Leftarrow \lambda_{a'b'}^{j'u} E_{wj'}^{a'b'} W_{v}^{w} {\Gamma_{\mu}}_{v}^{u} \;\; \forall\, a', b', w, j' \\
{R_\mu}_{ua'}^{wi'} &\Leftarrow \lambda_{a'}^{i'} E_{i'w}^{a'u} W_{v}^{w} {\Gamma_{\mu}}_{v}^{u} \;\; \forall\, u, a', w, i' \\
{R_\mu}_{a'u}^{wi'} &\Leftarrow \lambda_{a'}^{i'} E_{i'w}^{ua'} W_{v}^{w} {\Gamma_{\mu}}_{v}^{u} \;\; \forall\, a', u, w, i'
\end{aligned}$$

These R_μs are thus, the quantities to be constructed for solving the equations for λ_μ.

For the differentiation of Term 3B, it is simpler to think of the terms contributing to the differentiated composites de novo. Noting that we wish to generate composites of the de-excitation type, ie. ${R_\mu}_A^I$s we follow 3 steps:

Step 1: The possible structures for the differentiated $W_{\mu\mu}$s are constructed. See Fig. 5.2.8.

Step 2: The terms possible for generating $\{\overbrace{e^{T_\mu}W}{}_{\mu\mu}\}$ are constructed. Note that the

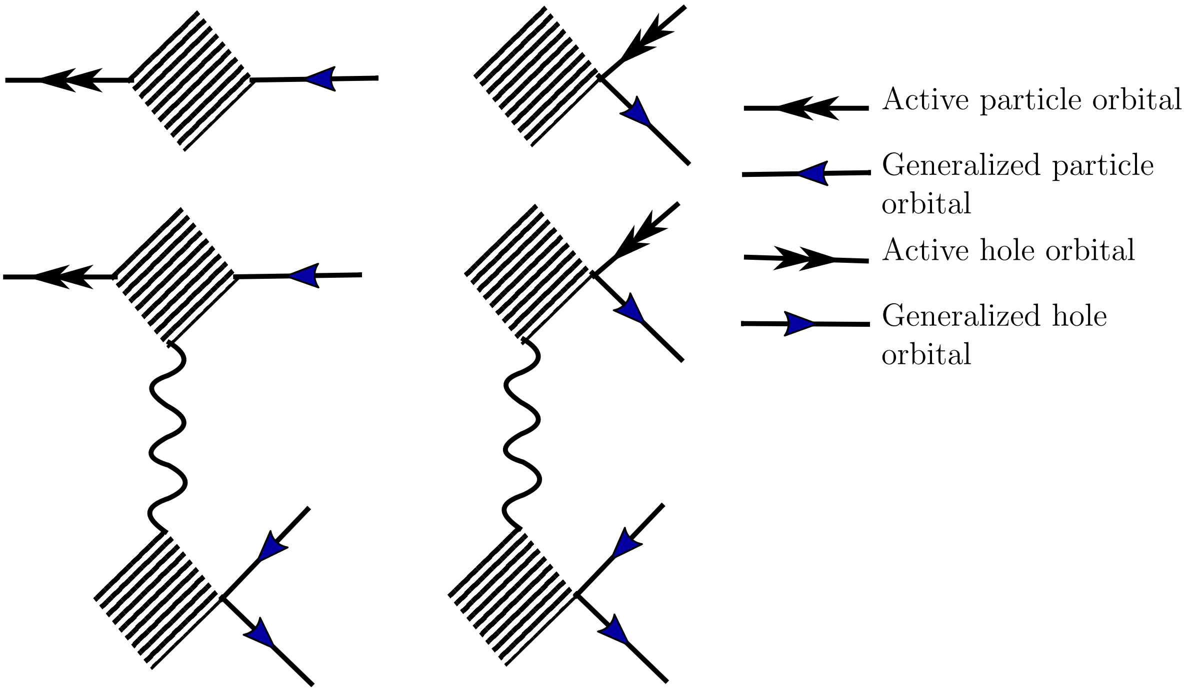

Figure 5.1: **Structures of the differentiated $W_{\mu\mu}$, removing the operator of the T_μ as well.**

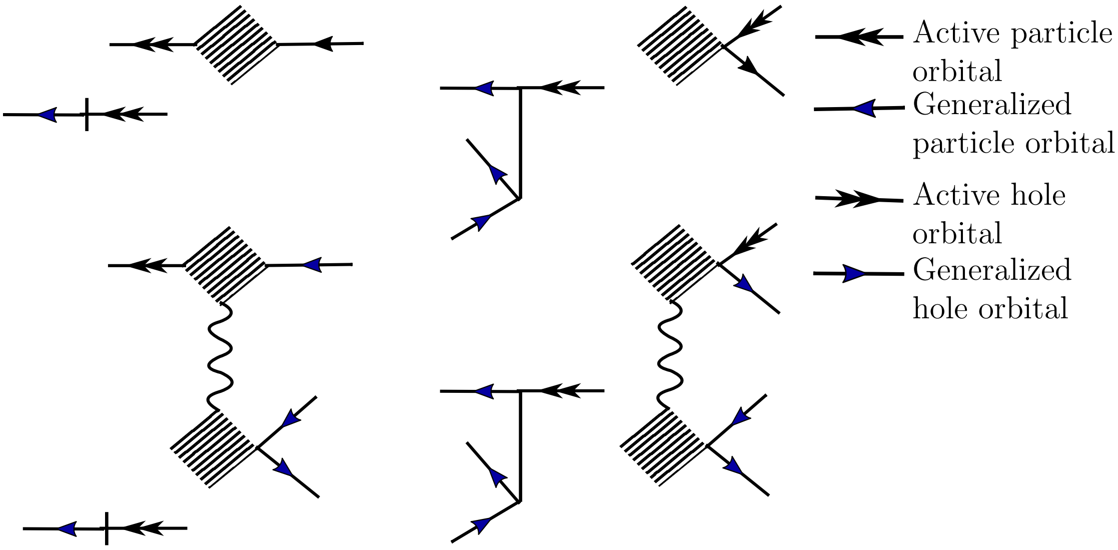

Figure 5.2: **Disconnected Structures of the T and differentiated $W_{\mu\mu}$.**

T_μs inside $W_{\mu\mu}$ in Term 3 are of two types: those which are solely connected to H inside $W_{\mu\mu}$ and those which are connected to both H and Λ_μ. When those T_μs of the second type which were the sole connectors to Λ_μ are differentiated, the corresponding terms contributing to ${R_\mu}_A^I$ look disconnected. Hence, such terms must also be constructed. See Fig. 5.1.

Step 3: The Λ_μs are then contracted with the composites generated in Steps 1 and 2. It is necessary to be careful that the open lines coming from Λ_μ are only of the active type as the differentiated T_μ from inside $W_{\mu\mu}$ could only have been originally connected to the $\Lambda_{\mu\mu}$ by active lines. The open inactive labels of ${R_\mu}_A^I$ can thus, come only from the Hamiltonian from inside $W_{\mu\mu}$.

The connected terms from the differentiation of Term 3B are enlisted below:

$$
\begin{aligned}
{R_\mu}_{a'}^{w} &\Leftarrow \sum_{u,d'} \lambda_{d'}^{w} T_{u}^{d'} \bar{H}_{a'}^{u} \quad \forall\ a', w \\
{R_\mu}_{a'}^{w} &\Leftarrow \sum_{u,d',c',k'} \lambda_{d'c'}^{wk'} T_{uk'}^{d'c'} \bar{H}_{a'}^{u} \quad \forall\ a', w \\
{R_\mu}_{a'}^{w} &\Leftarrow \sum_{u,d',c',k'} \lambda_{c'd'}^{wk'} T_{uk'}^{d'c'} \bar{H}_{a'}^{u} \quad \forall\ a', w \\
{R_\mu}_{a'}^{w} &\Leftarrow \sum_{u,c',k'} \lambda_{c'}^{k'} T_{uk'}^{c'w} \bar{H}_{a'}^{u} \quad \forall\ a', w \\
{R_\mu}_{a'}^{w} &\Leftarrow \sum_{u,c',k'} \lambda_{c'}^{k'} T_{uk'}^{wc'} \bar{H}_{a'}^{u} \quad \forall\ a', w \\
{R_\mu}_{a'b'}^{wj'} &\Leftarrow \sum_{u,c'} \lambda_{c'}^{w} T_{u}^{c'} \bar{H}_{a'b'}^{uj'} \quad \forall\ a', w, b', j' \\
{R_\mu}_{a'b'}^{wj'} &\Leftarrow \sum_{u,c'} \lambda_{c'd'}^{k'w} T_{uk'}^{d'c'} \bar{H}_{a'b'}^{uj'} \quad \forall\ a', w, b', j' \\
{R_\mu}_{a'b'}^{wj'} &\Leftarrow \sum_{u,c'} \lambda_{c'd'}^{wk'} T_{uk'}^{d'c'} \bar{H}_{a'b'}^{uj'} \quad \forall\ a', w, b', j' \\
{R_\mu}_{a'b'}^{wj'} &\Leftarrow \sum_{u,c',k'} \lambda_{c'}^{k'} T_{uk'}^{c'w} \bar{H}_{a'b'}^{uj'} \quad \forall\ a', w, b', j' \\
{R_\mu}_{a'b'}^{wj'} &\Leftarrow \sum_{u,c',k'} \lambda_{c'}^{k'} T_{k'u}^{c'w} \bar{H}_{a'b'}^{uj'} \quad \forall\ a', w, b', j'
\end{aligned}
$$

The terms are constructed by first generating $(\overbracket{\Lambda_\mu e^{T_\mu}})_{\mu\mu}$ (called temp_AA in the code) and then contracting with the differentiated $W_{\mu\mu}$. Only the active to active scattering of the $(\overbracket{\Lambda_\mu e^{T_\mu}})$ composite is required since all inactive labels can only come from inside

$W_{\mu\mu}$. The Eqs. (5.12) can then be written simply as:

$$
\begin{aligned}
R_{\mu}{}^{w}_{a'} &\Leftarrow \sum_{u} \mathit{temp\_AA}(w,u)\bar{H}^{u}_{a'} \ \ \forall\ a', w \\
R_{\mu}{}^{wj'}_{a'b'} &\Leftarrow \sum_{u} \mathit{temp\_AA}(w,u)\bar{H}^{uj'}_{a'b'} \ \ \forall\ a', w, b', j'
\end{aligned}
$$

Since this is only a 1p sector the fully de-excitation looking differentiated $W_{\mu\mu}$s can contribute to the disconnected terms. Explicitly:

$$
\begin{aligned}
R_{\mu}{}^{i'v}_{wu} &\Leftarrow \mathit{temp\_AA}(v,u)\bar{H}^{i'}_{w} \ \ \forall\ w, u, i', v \\
R_{\mu}{}^{i'j'v}_{wb'u} &\Leftarrow \mathit{temp\_AA}(v,u)\bar{H}^{i'j'}_{wb'} \ \ \forall\ w, b', u, i', j', v
\end{aligned}
$$

Once these $R_{\mu}{}^{I}_{A}$ are constructed they are projected from the right with the operators E^{A}_{I} of $T_{\mu}{}^{A}_{I}$. Only the projections compatible with the terms in the equation for T-amplitudes are carried out.

To construct the terms arising from terms I and II of $\mathcal{L}$, some careful considerations are required. If a vertex of $R_{\mu}{}^{I}_{A}$ comes entirely from Λ_{μ}, a right projection on it by a one-body excitation operator is a spurious term since no T can be solely connected with a Λ. There is no such term in the one body part of $R_{\mu}{}^{I}_{A}$ (subroutine *lamdiag_1b*) where a vertex comes entirely from lambda. The only possibility was $\Lambda_{2b} - WPH$ (WPH $\equiv \overline{H_{\mu_{PH}}}$) but by the solution of the T eq, WPH=0. There are two classes of diagrams in *lamdiag_2b*. One where a vertex of the full block comes solely from lambda (type A) and the other where both the vertices have at least one line coming from $\overbracket{He}^{T_{\mu}}$ (type B). The subroutine *lamdiag_2b_A* corresponds to the first class. Only the component of $R_{\mu}{}^{I}_{A}$, *delL2_A*, obtained from subroutine *lamdiag_2b_A* is to be used in projections where a one-body projection solely on one vertex occurs. This projection must be restricted to the second vertex as the first vertex is the one which comes solely from lambda (by choice).The subroutine *lamdiag_2b_B* corresponds to the second class of diagrams to give *delL2_B*. Both *delL2_A* and *delL2_B* are to be used in all other projections.

For the three-body G blocks, some special consideration is required for the term involving a disconnected L_2 as no T can be entirely connected to it. We enforce this by demanding that the vertices of $L2$ are not projected from the right. Thus, before carrying out the projections, we have 5 types of $R_{\mu}{}^{I}_{A}$:
delL1: One-body $R_{\mu}{}^{I}_{A}$
delL2_A: Unsymmetrized G block containing diagrams where the first vertex $(a \rightarrow i)$ of $(ab \rightarrow ij)$ comes solely from lambda
delL2_B: Symmetrized G block containing diagrams where each vertex has at least one line coming from $\overbracket{He}^{T_{\mu}}$

$delL3\_1$: Three-body $R_{\mu}{}^{I}_{A}$ where a two body projection from the right cannot be entirely on the first two vertices of the G-block

The same subroutines for projection equations for the T_μs can be used for projecting the Λ_μs by passing the transpose of the Λ arrays to the subroutines. The iterative procedure adopted for the equations for the Λ_μ is also the same as for the T_μs.

5.3 Computational Cost

The computational cost of UGA-SUMRCC at first glance is a multiple of the cost of a CCSD computation, the prefactor being the number of model space functions. The model space has a high scaling with number of active orbitals and electrons viz. $\sim N!$ for a CAS but being an effective Hamiltonian theory, large model spaces are anyhow unlikely to be feasible as a fallout of the intruder problem and this scaling is not expected to create a bottleneck. What could be of concern is the involvement of the three body G-blocks, the evaluation of which is the most expensive part of our computation. This has a cost of 12 $nact^2$ times a CCSD computation where 'nact' is the number of active orbitals and there are 12 possible three body structures for the G blocks. The number of unknowns scale as $N_{gh}^4 N_{gp}^2$ where gh (generalized hole) = No. of occupied orbitals + No. of active orbitals and gp (generalized particle) = No. of unoccupied orbitals + No. of active orbitals. Thus, at each iteration the scaling of the computational cost with the number of basis functions, N, is dominated by the terms containing the all-particle integrals, VPPPP in the expressions for the two-body and three-body G-blocks. The computational cost of UGA-QFMRCC must be studied stepwise. The first step is simply a CCSD calculation. The next step of determining the S_μ amplitudes has the same cost as UGA-SUMRCC. The overall scaling behavior of our UGA-QFMRCC is in fact of the same order as those in EIP or STEOM-CC except that the STEOM-CC ignores the three-body excitation operators necessary for equivalence, of physics incorporated, with our UGA-QFMRCC as mentioned in Sec. 3.2. This is one approximation among many which are open to us as well but due to the compact μ-dependent representation of the cluster operators, it was not necessary for us to try it. Since, these theories provide multiple roots without superfluous cost, we believe that it is workable for small to medium molecules or correlation sensitive parts of larger molecules in situations where accuracy takes precedence over cost.

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Chapter 6

Summary and Future Outlook

6.1 Summary

In this thesis we have introduced a simple and efficient spin-free JM-like Ansatz to formulate a spin-free SUMRCC theory called UGA-SUMRCC [1] for describing states dominated by one particle, one hole, or hole-particle excited reference functions relative to a closed shell ground state and a corresponding theory for energy differences called UGA-QFMRCC [2]. Our spin-free formulations automatically lead to wave-functions with definite spins without spin contamination. The functions in the model space are CSFs, $\{\phi_\mu\}$ rather than determinants and we choose them to span the Gel'fand basis. The virtual functions, χ_μ^l are generated by the actions of appropriate spin-free unitary generators, $\{E_\mu^l\}$ on ϕ_μ. These excitation operators are non-commuting which makes the associated cluster operators non-commuting in general, thereby making the expression for the direct term of the SUMRCC equations non-terminating. We have thus chosen a normal-ordered Ansatz for the wave operator, $\Omega_\mu = \{e^{T_\mu}\}$ where the normal ordering is with respect to a closed shell reference (vacuum state) to restore, operationally speaking, the commutativity of the cluster operators. Since there are no $T_\mu - T_\mu$ contractions in $\{e^{T_\mu}\}$, for T_μs with valence destruction operators, the powers of T_μ with these excitations would terminate when the power of T_μ is such that all the valence occupancies in ϕ_μ are exhausted. This is unlike the property of an ordinary exponential, e^{T_μ}, where the $T_\mu - T_\mu$ contractions allow the powers of T_μ to generate non-vanishing excitations out of ϕ_μ. Interestingly, the loss of clustering resulting from this deviation from a full exponential Ansatz is somewhat offset by the appearance of a so-called folded or coupling term which reintroduces a major portion of the T-T contracted terms. We have derived the working equations for the cluster amplitudes and of the effective Hamiltonian and proved the size extensivity of the theory. The working equations involve spin-free RDMs and lead to potentially disconnected amplitudes and hence, the proof of size-extensivity has to not only involve the proof of connectivity of the equations but also indicate how that translates into extensivity. In the specific equations used in this thesis we have demonstrated that the extensivity is retained in spite of using the projection equations which involve reduced density matrices (RDMs). The formalisms developed in this thesis have been applied to excited and electron attached/detached states relative to a closed shell ground state for some prototypical systems.

In our formulation and implementation of the UGA-SUMRCC and UGA-QFMRCC for excitation energies (EE), the model functions chosen by us are incomplete. This warrants the abandoning of the customary choice of intermediate normalization of the wave operator, and we have thoroughly discussed the modifications necessary for the formulation as well as the implementation.

In our most rigorous formulation there are no redundancies in the cluster amplitudes and we have discussed our specific choices for selecting the proper combinations of cluster operators needed to span the singles-doubles excitation sub-space of the set $\{T_\mu\} |\phi_\mu\rangle$. Alongside this development, we have also explored the possibility of using linearly dependent operators and providing equations for them via sufficiency conditions. This leads to simplification of the structure of the working equations but the results indicate that the performance is less uniform than the original rigorous scheme. A third avenue we have explored is to use amplitude equations directly whence the linear dependence of the excited functions does not play any significant role. We find that the amplitude equations show a stable performance across different molecular states but are deficient in terms of physical interactions included which manifests as marginally larger errors than the rigorous scheme. The trends are similar for UGA-SUMRCC and UGA-QFMRCC.

The most prominent strength of our theory appears to be the mechanism for orbital relaxation. We find that we are able to describe core electron ionization and excitations which are accompanied by very strong orbital relaxations and correlation relaxations in an accurate manner while using the orbitals of the corresponding closed shell ground states. We have exploited this strength by applying our theory in this domain. Moreover, to study the scalar relativistic effects on the ionization of the 1s core electrons of molecules containing medium heavy atoms, we have employed the spin-free four component Dirac-Hartree-Fock Hamiltonian. We find that the relativistic contribution to the ionization energy of the 1s electron increases with increasing atomic weight as expected but the accuracy of our theories remains consistent.

We have also formulated the analytic gradients for the single CSF limit of our UGA-SUMRCC theory called as UGA-OSCC theory and indicated the non-trivial aspects of its implementation. Computation of electric properties of some radicals via the use of numerical gradients with zero-field orbitals indicate that the analytic gradients would also provide numbers of comparable accuracy at lower cost.

6.2 Future Outlook

Future developments of the theories developed in this thesis may be in several directions. A limitation of both the UGA-SUMRCC and the UGA-QFMRCC theories lies in that they are effective Hamiltonian theories and are thus prone to the problem of encountering intruder states. One may wonder whether casting the coupled-cluster equations in an effective CI-like structure, as for example what was shown to be rather effective in the FS-MRCC theory via the Eigenvalue Independent Partitioning Technique [3] or the allied Intermediate Hamiltonian formalism [4, 5], could be a viable way to achieve stability of the target energies even in the presence of intruders. Of course, unlike in the FS-MRCC theory, the μ dependence of the cluster amplitudes would make the CI-like transcription somewhat more involved. We hope to carry out such studies in future. We are also now proceeding to higher valence sectors which is a fairly straightforward exercise if one adopts the method of amplitude equations. This would enable us to treat excited states dominated by doubly excited configurations which continue to be a challenge for linear response based approaches. The analytic gradients of the UGA-OSCC theory also hold much promise which we did not numerically implement in the thesis. However, we will apply it to prototypical systems in the very near future. An application of these theories to the computation of spin-sensitive properties is also being envisaged, where the absence of spin-contamination in the zeroth order correlated wave-function may be expected to both enhance the accuracy of the computed properties and to provide a compact formulation of the problem. One can also improve the applicability of these theories to heavy atom containing molecules wherein spin-orbit coupling effects become relevant by considering the spin-orbit coupling as a perturbation on the spin-free starting function. In conclusion, we may say that the formulation of these theories have opened up several avenues of exploration and we are continuing in our endeavors to study them as completely as possible and improve them where necessary.

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Appendix 1

VUMRCC

Let us consider a partitioning of our N-electron problem into an $N_c + N_v$ electron problem where N_c is the number of core electrons which form a doubly filled common part of all the model functions for all the valence-sectors and hence do not participate in static correlation while N_v is the number of valence electrons sub-sets of which when arranged in the active orbitals (n_v in number) in different ways generate the model functions for all the valence sectors. What do we mean by "valence sector" ? The closed shell function containing $N_c + N_v$ electrons may be called the (0,0) valence sector. All functions containing $N_c + (N_v - 1)$ electrons where an electron has been removed from an "active" orbital belong to the (1,0) valence sector, ie. (1-hole, 0-particle) valence sector. Similarly, all functions containing $N_c + (N_v + 1)$ electrons where an electron has been added to an "active" orbital belong to the (0,1) valence sector and so on. Starting from an $N_c + N_v$ problem it is possible to find all correlated functions having N_c electrons to $N_c + N_v + 2 * n_v$ electrons using the VU Ansatz which includes our targeted $N_c + N_v$ electron problem as the (1,1) valence sector. It is not essential to select the (0,0) sector as the $N_c + N_v$ closed shell function. Any suitable choice may be made. For example, if the N_c electron closed shell function is the (0,0) sector, our target $N_c + N_v$ electron sector would be the (0,N_v) valence sector. Notice that we have generated much more information than we had asked for. Is this a blessing or a curse ? Before we answer this let us look at the method of solution of the VUMRCC equations and the details of the proposed Ansatz.

Taking a cue from the SRCC equations, Mukherjee et al proposed an analogous

Ansatz for VUMRCC in 1975 as:

$$\Omega = \exp(T) \tag{A.1}$$

The set of model functions can be denoted as $\{\phi_\mu^{N_v}\}$ with the starting function as $\psi_{0k}^{N_v} = \sum_\mu \phi_\mu^{N_v} c_{\mu k} \forall k = 1, N_d$. The multi-reference description of a target state is limited to the valence sector to which it belongs. Incorporation of static correlation across valence sectors is not possible. Hence, we must carefully choose the (0,0) sector such that all the model functions important for static correlation are considered in the same valence sector. Say, our target valence sector is (m,n). Then, the Bloch equation which can be thought of as a multi-root generalization of the Schrodinger equation takes the form,

$$H\Omega P^{(m,n)} = \Omega P^{(m,n)} H_{eff} P^{(m,n)} \forall m, n \tag{A.2}$$

where,

$$H_{eff} = (P^{(m,n)} \Omega P^{(m,n)})^{-1} P^{(m,n)} H \Omega P^{(m,n)} \forall m, n \tag{A.3}$$

The T-operators are independent of the projectors $P^{(m,n)}$ and have the form:

$$T = \sum_{mn} T^{(m,n)} \tag{A.4}$$

Projecting the excited functions, $\chi_l^{N_v}$ on Eq. (A.2) after pre-multiplying with Ω^{-1}, we get the working equation,

$$\langle \chi_l^{N_v} | \overline{H} | \phi_\mu^{N_v} \rangle = 0 \tag{A.5}$$

where,

$$\overline{H} = \exp(-T) H \exp(T) \tag{A.6}$$

We see here that the unknowns are all T-amplitudes from (0,0) to (m,n) sectors which are solved in a coupled manner through Eq. (A.5). Since, the T-operators are normal ordered with respect to the selected core, the active orbitals can occur as both creation and annihilation operators making the T-operators non-commuting. As a result, $\overline{H}$ may contain a term like Fig. A.1 where a (0,1) sector T contributes to the equation for a (0,0) sector T. This is a confusing feature of the formalism as it appears physically improbable that the knowledge of correlation of an $N_c + 1$ electron system would be required to model the correlation of an N_c electron system. This theory however has no redundant operators and is solved as a matrix equation or projection equation with as many T-operators as there are linearly independent excited functions.

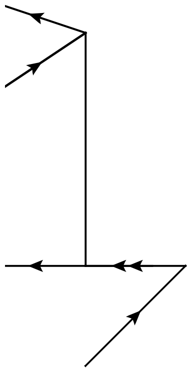

Figure A.1: (0,1) sector T contributes to the equation for a (0,0) sector T for $\Omega = \exp(T)$

In 1978, Lindgren proposed an Ansatz for VUMRCC of the form:

$$\Omega = \{\exp(T)\} \tag{A.7}$$

where {..} denotes normal ordering of the Ansatz with respect to the core, thereby ensuring commutativity of the T-operators. He also showed that it was possible to cast the VUMRCC equations as operator equations making the equations simpler. However, he was confronted with the problem of a linearly dependent set of operators. For example, T_i^a and T_{iu}^{au} are linearly dependent. T_{iu}^{au} is called an operator with a "direct spectator". There could only be one equation but if one was to use operator equations there would have to be separate equations for the two variables or you had to remove one. Since removing the linearly dependent operators went against the spirit of the Ansatz where T_{iu}^{au} is essential to model the change in T_i^a say, on removing an electron from 'u' for the (1,0) sector or adding an electron to 'u' for the (0,1) sector, Lindgren suggested that sufficiency conditions be invoked and T_i^a and T_{iu}^{au} be solved separately. The normal ordering of the Ansatz made a significant improvement on the theory by Mukherjee in that it ensured the removal of T-T contraction and removed the unappealing feature of higher valence sector T operators contributing to lower valence sector equations. What was thought of as sufficiency conditions by Lindgren was soon identified by Mukherjee as a so-called "Sub-system Embedding Condition" (SEC) rather than a sufficiency. The SEC implied that in order to solve a problem for a certain valence sector one had to systematically proceed from solution of the (0,0) sector across all intermediate sectors until the target sector. At each level the parameters already determined in the lower sector enter the equations as fixed values.

This discovery gave the VUMRCC its current widely accepted form. The procedure for solution of a (1,1) sector problem is illustrated in Fig.A.2.

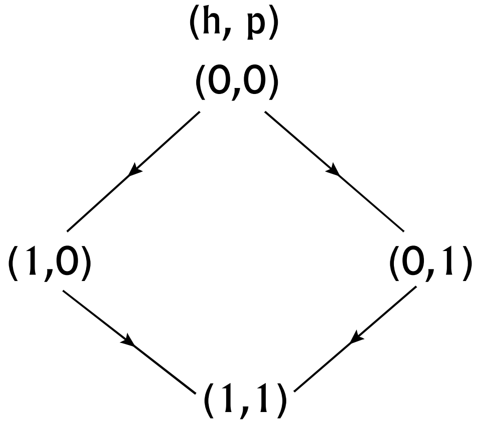

Figure A.2: Sub-system embedding for (1, 1) sector

Appendix 2

The Intruder Problem

The so-called "Intruder Problem" is a major drawback of any CAS based theory especially when it tries to construct a PES. Among the MRCC theories, VUMRCC and SUMRCC encounter this problem more often than not. The energies of all N_d roots are obtained in such theories by diagonalizing an effective Hamiltonian of dimension N_d. The problem stems from the fact that the functions in a CAS may not and generally will not be a reasonable description of all the roots of the problem. The diagonalization mixes all the functions and hence, the poorly described roots would spoil the accuracy of even the root which is well described in the CAS. To further illustrate the problem, let us take a specific example depicted in Fig. B.1. Let, σ_g^2 and σ_u^2 be 2 functions in a CAS where one of the roots, specifically the ground state is multi-reference at dissociation having contributions from the 2 model functions σ_g^2 and σ_u^2. Thus, in order to plot a PES for the ground state we require static correlation between σ_g^2 and σ_u^2. However, near equilibrium, the ground state is largely single reference and well described by σ_g^2. The model function σ_u^2 at equilibrium may be very much higher in energy than σ_g^2 and in fact, closer to some excited function, χ_m reached by a T-operator. In this situation the T-amplitude, $t_{\sigma_u}^m$ would be very large and could jeopardize the convergence of the non-linear set of T-amplitude equations even before we get to the diagonalization step ! Even if we manage to converge the T-amplitudes, the accuracy of the ground state would be spoilt by the poorly described higher root.

An extreme case of the intruder problem arises at curve crossings. The expression

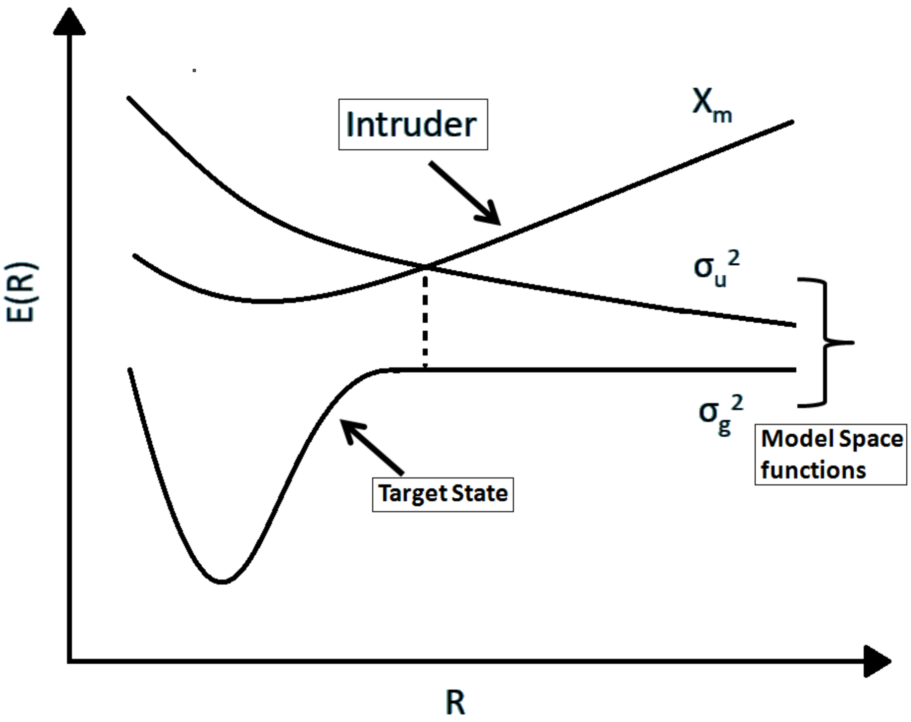

Figure B.1: The Intruder Problem

for H_{eff} correct up to second order is given by:

$$H_{eff\mu\nu}{}^{(2)} = \sum_{l} \langle \phi_\mu | H | \chi_\nu^l \rangle \Omega_\nu^{l\,(1)} + H_{\mu\nu} \tag{B.1}$$

where,

$$\Omega_\nu^{l\,(1)} \sim \frac{\langle \chi_l | H | \phi_\nu \rangle}{E_\nu^0 - E_l^0} \tag{B.2}$$

At the point of curve crossing between χ_l and ϕ_ν, $\Omega_\nu^{l\,(1)}$ becomes singular and ${H_{eff}}^{(2)}$ becomes indeterminable although the root dominated by ϕ_μ which is say, the ground state, is still perfectly well-described. Using IMS may sometimes solve the problem but selecting an IMS that is balanced for all roots across the entire PES is, in general, difficult.

Appendix 3

Normalization of the Wave Operator

The normalization of Ω plays an important role in the details of a theory and can affect issues like size extensivity. There are three alternatives that have been pursued. With reference to Eq. (A.3) we see that the expression for H_{eff} takes the simplest form if we choose Ω such that $P\Omega P = P$. This is called *Intermediate Normalization* (IN). Using IN with CAS is the most common choice. It was shown by Mukherjee that if IN was used with an IMS, the theory lost size extensivity and the only way to restore it was to abandon IN and use the value of $P\Omega P$ as is.

The second is the *Unitary Normalization* where:

$$\Omega^{-1} = \Omega^{\dagger} \tag{C.1}$$

This implies,

$$\overline{H}_{QP} = \overline{H}_{PQ} = 0 \tag{C.2}$$

As suggested by Kemble, this is the minimal condition for Ω. But, it does impose any condition on the value of $P\Omega P$ and one is free to proceed as before. The third option is the *Jørgensen Normalization* which proposes that we only ensure that $\overline{H}_{PP}$ is Hermitian but do not constrain $\overline{H}_{QQ}$. Thus, Ω is parametrized separately for the "closed" components as X and "excited" components as T.

$$\Omega = \{\exp(T + X)\} \tag{C.3}$$

$$P\Omega^\dagger\Omega P = P \tag{C.4}$$

$$\Omega P = P + \Omega_{ex}P + \Omega_{cl}P \tag{C.5}$$

We use Eq. (C.4) in Eq. (C.5) to determine Ω_{cl}. The unitary normalization and Jørgensen normalization lead to size extensive equations even for IMS.

Appendix 4

Emergence of e^{θ}

A normal-ordered product of two operators, $\{e^{T}X\}$ can be written as a product of two normal-ordered operators, $\{e^{T}\}\{Y\}$ by using the Wicks' theorem in reverse. Y consists of various terms with contractions between powers of T with X. It is a property of an exponential operator that the operators left behind after its contraction with another operator, say, X in this case, can be grouped back into an exponential structure. This leads to the recursive generation of a series of terms when one applies Wicks' theorem in reverse successively on $\{e^{T}X\}$ as shown in Eqs. D.1-D.4. In this appendix we show how this series can be compactly written as $\{e^{T}\}\{\overbracket{e^{\theta}X}\}$ where θ is a power series in T where every term is connected. This provides the expression for $\{Y\}$ as $\{e^{T}\}\{\overbracket{e^{\theta}X}\}$. We refer to $\{e^{T}\}\{X\}$ as the 0th generation term and each subsequent application of the Wicks' theorem in reverse increases the generation of the terms.

$$\{e^{T}X\} = \{e^{T}\}\{X\} - \{e^{T}\overbracket{e^{T}X}\} \tag{D.1}$$

$$= \{e^{T}\}\{X\} - \{e^{T}\}\{\overbracket{e^{T}X}\} + \{e^{T}\overbracket{e^{T}\overbracket{e^{T}X}}\} \tag{D.2}$$

$$= \{e^{T}\}\{X\} - \{e^{T}\}\{\overbracket{e^{T}X}\} + \{e^{T}\}\{\overbracket{e^{T}\overbracket{e^{T}X}}\} - \{e^{T}\overbracket{e^{T}\overbracket{e^{T}\overbracket{e^{T}X}}}\} \tag{D.3}$$

$$= \{e^{T}\}\{X\} - \{e^{T}\}\{\overbracket{e^{T}X}\} + \{e^{T}\}\{\overbracket{e^{T}\overbracket{e^{T}X}}\} - \{e^{T}\}\{\overbracket{e^{T}\overbracket{e^{T}\overbracket{e^{T}X}}}\} + \ldots \tag{D.4}$$

$$\tag{D.5}$$

Power of T	0	1	2	3
Gen 0	1			
Gen I		$-TX$	$-\frac{1}{2}TTX$	$-\frac{1}{6}TTTX$
Gen II			TTX	$\frac{1}{2}TT(TX) + \frac{1}{2}T(TTX)$
			TTX	$\frac{1}{2}TT(TX) + \frac{1}{2}TT(TX) + \frac{1}{2}T(TTX) + \frac{1}{2}T(TTX)$
Gen III				$-TTTX$
				$-TTTX$ $-TTTX$ $-TTTX$
				$-TTTX$
Overall term	1	$-TX$	$\frac{1}{2}TTX + TTX$	$-\frac{1}{6}TTTX$ $-TTTX$ $-TTTX$

Table D.1: Terms of various topologies arising from the expansion of $\{e^T X\}$ at various generations with the corresponding factors indicating the emergence of e^θ

We now collect terms having the same power of T contracted to X from the various generations. The operator X plays a pivotal role in determining the topology of the connectivity of the T operators. Only those terms can be clubbed together which have the same connectivity with X. The possible terms for each power of T have been tabulated in Table D with terms having the same topology in the same row. The factors accompanying the terms of various topologies indicate the emergence of an exponential structure for the composite connected to X, which we call e^θ. Then, we can easily see that θ itself is also a series of connected operators:

$$\theta = -T + TT - TTT + ... \tag{D.6}$$

Appendix 5

Connectivity of the Projection Equations

We have shown in Sec. 2.3.1, that the composites G_μ featuring in the projection equations are connected. By an analysis of the explicit working equations we have used, we have been able to prove the size-extensivity of the UGA-SUMRCC and UGA-QFMRCC theories. However, in a general analysis without considering the linear dependence or independence of the excitation manifold, it is possible to demonstrate the connectivity of the working equations. This can be achieved by a cumulant decomposition of the spin-free RDMs [1, 2] featuring in the projection equations. We first note that the various ranks n of $G_\mu^{l(n)}$, can contribute to a matrix element, $\langle\chi_\mu^l|G_\mu^l|\phi_\mu\rangle \equiv \langle\chi_\mu^l|\sum_n G_\mu^{l(n)}|\phi_\mu\rangle$. Using Eq. 2.6 we may express the matrix elements as expectation values with respect to ϕ_μ :

$$\langle\chi_\mu^l|\sum_n G_\mu^{l(n)}|\phi_\mu\rangle = \langle\phi_\mu|\{\epsilon_\mu^l\}^\dagger \sum_n G_\mu^{l(n)}|\phi_\mu\rangle \ \equiv \langle\phi_\mu|\{\epsilon_l^\mu\}\sum_n G_\mu^{l(n)}|\phi_\mu\rangle \tag{E.1}$$

Using Wick's theorem to rewrite the product of $\{\epsilon_l^\mu\}$ with those appearing in $G_\mu^{l(n)}$, it is easy to see that the only non-zero contribution to the matrix element comes from the terms which are either completely contracted or those involving generators of the unitary group with active labels only. The latter will give rise to RDMs of various ranks dependent on the rank of the generators of the unitary group with active labels. We note now that the set of active orbital labels destroyed by the generators of the unitary group must be the same as those created although they are not necessarily in the same order. For example, in the h-p sector, a $\phi_\mu \equiv \phi(I, A)$ with I referring to the active hole and A to the active particle orbital respectively, the non-zero 2-RDMs can only be Γ^{IA}_{IA} and Γ^{AI}_{IA}. We would henceforth refer to strict index equality in the lower and upper indices as *'diagonality'*. When the upper and lower index sets are equal but not all of the equal labels are in the same order in the upper and lower sets, we refer to this property as *'quasi-diagonality'*. Hence, Γ^{IA}_{IA} is diagonal and Γ^{AI}_{IA} is quasi-diagonal. In our UGA-MRCCs all density matrix elements are either diagonal or quasi-diagonal.

For the h-p model spaces studied by us here, the non-zero 2-RDMs are not always product separable and they may lead to disconnected pieces in various terms. The disconnected pieces appear when a part of the pairs of active orbitals appears only on the de-excitation part of the operator, $\{\epsilon_l^\mu\}$ and a part on the G-block or when all the pairs of active orbitals of the RDM come from the $\{\epsilon_l^\mu\}$ only . Representative diagrams for the first case are shown in Figs. E.1 and E.2. In a CCSD truncation scheme for a h-p quasi-complete model space, some active lines to the right may emanate from the G-block and have common labels with active lines to the left which may have arisen from the projection such as in Fig. E.2. Even though parts of the 2-RDM may occur on different factors ($\{\epsilon_l^\mu\}$ and $G_\mu^{l(n)}$) (as in Fig. E.2), they are by necessity quasi-diagonal and hence connected. As a consequence, when the factors $\{\epsilon_l^\mu\}$ and $G_\mu^{l(n)}$ each have a h-p pair on them, the labels on the h-p lines are the same leading to connected structures. A term like Fig. E.1 does not occur in our formulation, as we do not have T operators containing direct spectators and hence, there are no projection equations with $\{\epsilon_l^\mu\}$ having its adjoint structure. However, we do have the so-called exchange spectator operators and terms like Fig. E.3 arise which can apparently cause disconnected terms when the label, I, and the pair, i,a are on different molecular fragments.

Our intention is to demonstrate that one can eliminate the disconnected terms via cumulant decomposition.We shall show that the disconnected quantities for a given working equation get canceled on invoking the working equations for other, lower rank, t-amplitudes. In order to match terms between equations, it becomes necessary to decompose higher body densities into lower body densities via a so-called cumulant decomposition [1, 2]. We will also demonstrate that in order to factor out the lower body equation from the higher body equation in its entirety, we need to introduce terms containing higher body densities which are zero in value. The strategy used by us is general and may be suitably extended for analyzing the connectivity for general mh-np quasi-complete model spaces.

Using the general definition of a spin-free cumulant[1, 2], we have:

$$\begin{aligned}
\Gamma^{uv}_{wx} = {} & \langle\phi_\mu|\{E^u_w\}|\phi_\mu\rangle\langle\phi_\mu|\{E^v_x\}|\phi_\mu\rangle \\
& -\tfrac{1}{2}\langle\phi_\mu|\{E^u_x\}|\phi_\mu\rangle\langle\phi_\mu|\{E^v_w\}|\phi_\mu\rangle + \Lambda^{uv}_{wx} \qquad \text{(E.2)} \\
\Gamma^{xyz}_{uvw} = {} & \langle\phi_\mu|\{E^x_u\}|\phi_\mu\rangle\langle\phi_\mu|\{E^y_v\}|\phi_\mu\rangle\langle\phi_\mu|\{E^z_w\}|\phi_\mu\rangle \\
& -\tfrac{1}{2}\langle\phi_\mu|\{E^x_u\}|\phi_\mu\rangle\langle\phi_\mu|\{E^y_w\}|\phi_\mu\rangle\langle\phi_\mu|\{E^z_v\}|\phi_\mu\rangle + \langle\phi_\mu|\{E^x_u\}|\phi_\mu\rangle\Lambda^{yz}_{vw} \\
& -\tfrac{1}{2}\langle\phi_\mu|\{E^x_w\}|\phi_\mu\rangle\langle\phi_\mu|\{E^y_v\}|\phi_\mu\rangle\langle\phi_\mu|\{E^z_u\}|\phi_\mu\rangle + \langle\phi_\mu|\{E^y_v\}|\phi_\mu\rangle\Lambda^{xz}_{uw} \\
& -\tfrac{1}{2}\langle\phi_\mu|\{E^x_v\}|\phi_\mu\rangle\langle\phi_\mu|\{E^y_u\}|\phi_\mu\rangle\langle\phi_\mu|\{E^z_w\}|\phi_\mu\rangle + \langle\phi_\mu|\{E^z_w\}|\phi_\mu\rangle\Lambda^{xy}_{uv} \\
& +\tfrac{1}{4}\langle\phi_\mu|\{E^x_w\}|\phi_\mu\rangle\langle\phi_\mu|\{E^y_u\}|\phi_\mu\rangle\langle\phi_\mu|\{E^z_v\}|\phi_\mu\rangle \\
& +\tfrac{1}{4}\langle\phi_\mu|\{E^x_v\}|\phi_\mu\rangle\langle\phi_\mu|\{E^y_w\}|\phi_\mu\rangle\langle\phi_\mu|\{E^z_u\}|\phi_\mu\rangle + \Lambda^{xyz}_{uvw} \qquad \text{(E.3)}
\end{aligned}$$

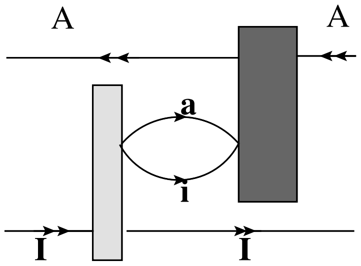

Figure E.1: Apparently disconnected term when I and A are on different fragments. We note here that the left-most projection operator is a de-excitation operator and is *not* associated with a connected amplitude. Hence, one would have to keep in mind that it is not a connected entity, unlike the G-blocks on the right. The same holds good for the de-excitation operators in Figs. E.2 and E.3.

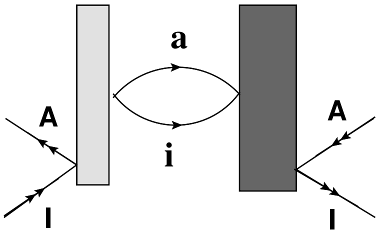

Figure E.2: Apparently disconnected term with quasi-diagonal RDM.

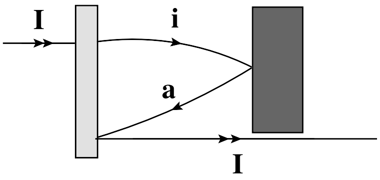

Figure E.3: Occurrence of disconnected RDM and excitation.

for arbitrary active indices u-z, which maybe holes or particles. We note here that for a general mh-np active situation, Λ is a connected quantity containing the exchange components of the product of one-body RDMs along with spatial cumulants. However, in our special 1h-1p situation, the prior quantities are zero and hence, we deal with cumulants only.

We define the 1h density matrix element η^I_I as: $\eta^I_I = \sum_\sigma = \langle \phi_\mu | I_\sigma I^\dagger_\sigma | \phi_\mu \rangle = -\langle \phi_\mu | \{E^I_I\} | \phi_\mu \rangle = 1$. γ^A_A is obviously equal to $\langle \phi_\mu | \{E^A_A\} | \phi_\mu \rangle = 1$. To calculate the values of the non-zero 2-body RDMs we note that:

$$\begin{aligned} \{E^{IA}_{IA}\} = &\quad \sum_{\sigma_1\sigma_2} \{I^\dagger_{\sigma_1} A^\dagger_{\sigma_2} A_{\sigma_2} I_{\sigma_1}\} \\ = &\quad -\sum_{\sigma_1\sigma_2} \{I_{\sigma_1} I^\dagger_{\sigma_1} A^\dagger_{\sigma_2} A_{\sigma_2}\} \\ = &\quad -\sum_{\sigma_1} I_{\sigma_1} I^\dagger_{\sigma_1} \sum_{\sigma_2} A^\dagger_{\sigma_2} A_{\sigma_2} \end{aligned} \tag{E.4}$$

and

$$\begin{aligned} \{E^{AI}_{IA}\} = &\quad \sum_{\sigma_1\sigma_2} \{A^\dagger_{\sigma_1} I^\dagger_{\sigma_2} A_{\sigma_2} I_{\sigma_1}\} \\ = &\quad \sum_{\sigma_1\sigma_2} \{A^\dagger_{\sigma_1} A_{\sigma_2} I_{\sigma_1} I^\dagger_{\sigma_2}\} \\ = &\quad \sum_{\sigma_1\sigma_2} A^\dagger_{\sigma_1} A_{\sigma_2} I_{\sigma_1} I^\dagger_{\sigma_2} \end{aligned}$$

It then follows that:

$$\begin{aligned} \Gamma^{IA}_{IA} = &\quad \langle \phi_\mu | \{E^{IA}_{IA}\} | \phi_\mu \rangle \\ = &\quad -\eta^I_I \gamma^A_A + \Lambda^{IA}_{IA} \end{aligned} \tag{E.5}$$

$$\begin{aligned} \Gamma^{AI}_{IA} = &\quad \langle \phi_\mu | \{E^{AI}_{IA}\} | \phi_\mu \rangle \\ = &\quad \tfrac{1}{2} \eta^I_I \gamma^A_A + \Lambda^{AI}_{IA} \end{aligned} \tag{E.6}$$

In order to get at the general case, we introduce the quantity, Λ^{IA}_{IA} although, we keep in mind that $\Lambda^{IA}_{IA} = 0$. The exchange cumulants encode spin correlation and their values may be obtained from:

$$\Lambda^{AI}_{IA} = \quad \langle \phi_\mu | \textstyle\sum_{\sigma_1 \neq \sigma_2} A^\dagger_{\sigma_1} A_{\sigma_2} I_{\sigma_1} I^\dagger_{\sigma_2} | \phi_\mu \rangle \tag{E.7}$$

For the h-p CSFs it then follows that Λ^{IA}_{IA} is zero and Λ^{AI}_{IA} is non-zero indicating that Γ^{AI}_{IA} is not exactly factorizable into products of lower body RDMs.

The explicit working equations for t_i^a, t_{iI}^{Ia} and t_{iA}^{Aa} operators in the 1h-1p sector are reproduced here from Eqs. 2.54, 2.55 and 2.56 for ease of reference:

$$\begin{aligned}
G_i^a - G_{iI}^{aI}\eta_I^I + G_{iA}^{aA}\gamma_A^A - \frac{1}{2}G_{iI}^{Ia}\eta_I^I - \frac{1}{2}G_{iA}^{Aa}\gamma_A^A + G_{iIA}^{aIA}\Gamma_{IA}^{IA} - \frac{1}{2}G_{iAI}^{AaI}\Gamma_{IA}^{IA}& \\
-\frac{1}{2}G_{iIA}^{IaA}\Gamma_{IA}^{IA} + G_{iIA}^{aAI}\Gamma_{IA}^{AI} - \frac{1}{2}G_{iIA}^{AaI}\Gamma_{IA}^{AI} - \frac{1}{2}G_{iAI}^{IaA}\Gamma_{IA}^{AI} = 0& \qquad \text{(E.8)} \\
G_i^a\eta_I^I - G_{iI}^{aI}\eta_I^I - G_{iA}^{aA}\Gamma_{IA}^{IA} + 2G_{iI}^{Ia}\eta_I^I - G_{iA}^{Aa}\Gamma_{AI}^{IA} + G_{iIA}^{aIA}\Gamma_{IA}^{IA} + G_{iIA}^{AIa}\Gamma_{IA}^{AI}& \\
-2G_{iIA}^{IaA}\Gamma_{IA}^{IA} + G_{iIA}^{aAI}\Gamma_{IA}^{AI} - 2G_{IiA}^{aAI}\Gamma_{IA}^{AI} + G_{iAI}^{IaA}\Gamma_{IA}^{IA} = 0& \qquad \text{(E.9)} \\
-G_i^a\gamma_A^A - G_{iI}^{aI}\Gamma_{IA}^{IA} - G_{iA}^{aA}\gamma_A^A - G_{iI}^{Ia}\Gamma_{AI}^{IA} + 2G_{iA}^{Aa}\gamma_A^A - G_{iIA}^{aIA}\Gamma_{IA}^{IA} + 2G_{iIA}^{AIa}\Gamma_{IA}^{IA}& \\
-G_{iIA}^{IaA}\Gamma_{IA}^{AI} - G_{iIA}^{aAI}\Gamma_{IA}^{AI} + 2G_{IiA}^{aAI}\Gamma_{IA}^{AI} + G_{iAI}^{IaA}\Gamma_{IA}^{IA} = 0& \qquad \text{(E.10)}
\end{aligned}$$

To ascertain the connectivity of the working equations, by the strategy delineated in the paragraphs above let us consider the specific example of the pair of projection equations for t_i^a and t_{iI}^{Ia}, ie. Eqs. E.8 and E.9. We note that the active label, I, in the de-excitation operator, E_{aI}^{Ii} will always contribute an RDM where 'I' will figure in both the upper and lower indices. Among the various terms generated in the projection equations, there will be some terms containing η_I^I while the rest of the terms will contain either Γ_{IA}^{IA} or Γ_{IA}^{AI}. The latter two can also be written in terms of factors η_I^I, γ_A^A and a cumulant, Λ, if we use Eqs. E.5 and E.6. Thus the entire set of projection equations can be grouped into two parts: in one η_I^I explicitly appears and in the other only Λ_{IA}^{IA} or Λ_{IA}^{AI} but no η_I^I appears. It is then possible to rewrite Eq. E.9 as:

$$\begin{gathered}
\eta_I^I[\boldsymbol{G_i^a} - G_{iI}^{aI} + 2G_{iI}^{Ia} + \gamma_A^A(\boldsymbol{-G_{iA}^{aA}} + G_{iIA}^{aIA} - 2G_{iIA}^{IaA} + G_{iAI}^{IaA}) \\
-\tfrac{1}{2}\gamma_A^A(\boldsymbol{-G_{iA}^{Aa}} + G_{iAI}^{AaI} + G_{iIA}^{aAI} - 2G_{iIA}^{AaI})] \\
\mathit{Term\ (i)} \\
+\Lambda_{IA}^{IA}(-G_{iA}^{aA} + G_{iIA}^{aIA} - 2G_{iIA}^{IaA} + G_{iAI}^{IaA}) + \Lambda_{IA}^{AI}(-G_{iA}^{Aa} + G_{iAI}^{AaI} + G_{iIA}^{aAI} - 2G_{iIA}^{AaI}) = 0 \\
\mathit{Term\ (ii)} \qquad \text{(E.11)}
\end{gathered}$$

We note that in Term (i) there are several components in which the pair of lines containing label, I, are generated exclusively from the de-excitation operator, E_{aI}^{Ii}. *These components are all disconnected, and they are all characterized by the property that the label, 'I', never appears in the associated G-blocks.* These disconnected entities have been shown in bold letters. It is remarkable that all the components in Term (i) appearing in the brackets, (...) in Eq. E.11 appear in Eq. E.8 which originates from the projection with E_a^i. However, there are more components in Eq. E.8 than what appears in Term (i). The missing entities in Term (i) are those in Eq. E.8 which contain: (a) η_I^I and (b) the 2-RDMs, Γ_{IA}^{IA} and Γ_{IA}^{AI} . These terms obviously cannot appear in Term (i), since this would have required a cumulant decomposition of a 2-RDM, Γ^{II}_{II} for (a) and 3-RDMs in Eq. E.9 containing at least one 'I' in both its upper and lower indices. For h-p CSFs, Γ^{II}_{II} and all the 3-RDMs are zero since such density matrices would have violated the exclusion principle in a ϕ_μ where there are only single active hole and particle occupancies labeled by I and A respectively. In order to complete the appearance of all components of Eq. E.8 in Term (i), we add to Eq. E.9 all those components which contain Γ^{II}_{II} and 3-RDMs which do not change the equation since they are all zero in value. We thus add the following sum of components each of which is individually zero:

$$-G^{Ia}_{iI}\Gamma^{II}_{II}, -G^{AaI}_{iAI}\Gamma^{AII}_{IAI}, -G^{aIA}_{iIA}\Gamma^{IAI}_{IAI}, -G^{aAI}_{iIA}\Gamma^{IAI}_{IIA}, -G^{AaI}_{iAI}\Gamma^{IAI}_{IAI}, -G^{IaA}_{iIA}\Gamma^{AII}_{IAI}, -G^{IaA}_{iAI}\Gamma^{AII}_{IAI} \tag{E.12}$$

Eq. E.9 thus becomes:

$$\begin{gathered}
G^{a}_{i}\eta^{I}_{I} - G^{aI}_{iI}\eta^{I}_{I} - G^{aI}_{iI}\Gamma^{II}_{II} - G^{aA}_{iA}\Gamma^{IA}_{IA} + 2G^{Ia}_{iI}\eta^{I}_{I} - G^{Ia}_{iI}\Gamma^{II}_{II} - G^{Aa}_{iA}\Gamma^{IA}_{AI} \\
+G^{aIA}_{iIA}\Gamma^{IA}_{IA} + G^{AIa}_{iIA}\Gamma^{AI}_{IA} - 2G^{IaA}_{iIA}\Gamma^{IA}_{IA} + G^{aAI}_{iIA}\Gamma^{AI}_{IA} - 2G^{aAI}_{IiA}\Gamma^{AI}_{IA} + G^{IaA}_{iAI}\Gamma^{IA}_{IA} \\
-G^{AaI}_{iAI}\Gamma^{AII}_{IAI} - G^{aIA}_{iIA}\Gamma^{IAI}_{IAI} - G^{aAI}_{iIA}\Gamma^{IAI}_{IIA} - G^{AaI}_{iAI}\Gamma^{IAI}_{IAI} - G^{IaA}_{iIA}\Gamma^{AII}_{IAI} - G^{IaA}_{iAI}\Gamma^{AII}_{IAI} = 0
\end{gathered} \tag{E.13}$$

The cumulant decomposition of the zero RDMs would generate either a product of cumulants containing an η^{I}_{I} and some 2-Λ or, a product of 1-RDMs, one of which would be η^{I}_{I} or, a 3-Λ. In fact, the cumulant decomposition of the associated zero 2- and 3-RDMs have the expressions:

$$\Gamma^{II}_{II} = \quad 0 = \tfrac{1}{2}\eta^{I}_{I}{}^{2} + \Lambda^{II}_{II} \tag{E.14}$$

$$\Gamma^{AII}_{IAI} = \quad 0 = -\tfrac{1}{4}\eta^{I}_{I}{}^{2}\gamma^{A}_{A} - \eta^{I}_{I}\Lambda^{AI}_{IA} + \Lambda^{IAI}_{AII} \tag{E.15}$$

$$\Gamma^{IAI}_{IAI} = \quad 0 = \tfrac{1}{2}\eta^{I}_{I}{}^{2}\gamma^{A}_{A} - 2\eta^{I}_{I}\Lambda^{IA}_{IA} + \gamma^{A}_{A}\Lambda^{II}_{II} + \Lambda^{IAI}_{IAI} \tag{E.16}$$

Using the expressions above, we can include the missing components of Eq. E.8 in Term (i) (to be henceforth called modified Term (i)) and club the rest of the contribution of Eq. E.12 into Term (ii) (to be henceforth called modified Term (ii)). We show explicitly only the terms containing two body G-blocks to avoid complexity. The decomposition of the higher body densities using Eqs. E.14-E.16 can be similarly carried out.

$$\begin{gathered}
\eta^{I}_{I}[G^{a}_{i} - G^{aI}_{iI}\eta^{I}_{I} + G^{aA}_{iA}\gamma^{A}_{A} - \tfrac{1}{2}G^{Ia}_{iI}\eta^{I}_{I} - \tfrac{1}{2}G^{Aa}_{iA}\gamma^{A}_{A}] \\
Modified\ Term\ (i) \\
+(\tfrac{1}{2}\eta^{I2}_{I} - \eta^{I}_{I} - \Lambda^{II}_{II})G^{aI}_{iI} + (-\tfrac{1}{2}\eta^{I2}_{I} + 2\eta^{I}_{I} - \Lambda^{II}_{II})G^{Ia}_{iI} - \Lambda^{IA}_{IA}G^{aA}_{iA} - \Lambda^{AI}_{IA}G^{Aa}_{iA} = 0 \\
Modified\ Term\ (ii)
\end{gathered} \tag{E.17}$$

Owing to the validity of Eq. E.8, the entire modified Term (i) vanishes making Eq. E.9 reduce to just the modified Term (ii) for up to two body G-blocks:

$$(\frac{1}{2}\eta_I^{I2} - \eta_I^I - \Lambda_{II}^{II})G_{iI}^{aI} + (-\frac{1}{2}\eta_I^{I2} + 2\eta_I^I - \Lambda_{II}^{II})G_{iI}^{Ia} - \Lambda_{IA}^{IA}G_{iA}^{aA} - \Lambda_{IA}^{AI}G_{iA}^{Aa} = 0 \quad \text{(E.18)}$$

Since, 2- and 3-Λs are all connected quantities, Eq. E.9 written in terms of the cumulants, Λ, consists entirely of connected terms. Some components in the modified Term (ii) contain only 3-Λs and their connectivity ensures that each such component is connected. There would also be some contribution coming from products of γ_A^A and a 2-Λ where the γ_A^A always occurs on the G-block. Hence these components are also connected. By an entirely similar reasoning, Eq. 2.61 involving the de-excitation operator E_{aA}^{Ai} upon cumulant decomposition would also reduce to a set of connected components involving cumulants after invoking Eq. E.8. Here the roles of γ_A^A and η_I^I would be interchanged. Moreover, also for true excitations involving active orbitals (such as $I \rightarrow a$ or $i \rightarrow a$) the projection equations involving an exchange spectator scattering in the de-excitation operator can be similarly transformed into a set of connected components containing the appropriate 2-Λs and 3-Λs. The disconnected components along with several other connected components and appropriate densities vanish because of the validity of the lower body equations without the spectators. Turning now to the 1-body projection equations, the uncontracted active lines in a composite may appear either entirely on the G-block which is explicitly connected or one on the projection and the other on the G-block. In the latter case diagonality/quasi-diagonality of RDMs ensures that they are connected since the active line on the de-excitation operator would have one label in common with one of those occurring on the G-block.

It is interesting to note that, the proof of the connectivity brought to the fore the use of 2- and 3-Λs having indices for which the corresponding 2- and 3-Γs vanish due to the Pauli Exclusion principle. This is clearly demonstrated in Eqs. E.14, E.15 and E.16 above. We may call such cumulants as Exclusion Principle Violating (EPV) Λs. For the h-p case at the CCSD level of truncation, the connected expressions will contain up to 3-Λs. For higher truncation schemes, 4- and higher rank Λs can also appear.

The decomposed working equations (for example, Eq. E.18) are reminiscent of the expressions one would obtain using Ts in Generalized Normal Ordering (GNO) introduced by Mukherjee [1] and further elaborated by Kutzelnigg and Mukherjee [2]. We may then envisage that an Ansatz of the form:

$$\Omega_\mu = \{e^{\{T\}_\mu}\} \quad \text{(E.19)}$$

where the cluster operators for each model function, ϕ_μ, are written in GNO with respect to ϕ_μ may lead to a more compact representation of the working equations. The

GNO for spinorbitals, written with respect to an MR state, ψ_0, has two properties: (i) the operators anti-commute under GNO and (ii) the expectation value of an operator in GNO with respect to ψ_0 vanishes. We denote by the symbol, $\{...\}_\mu$, a product in GNO with respect to ϕ_μ. The usual curly bracket notation, $\{...\}$, is still reserved for an ordinary normal-ordered product. We do not want to elaborate on this strategy any further in this thesis.

The same conclusions could have been drawn by an alternative but equivalent strategy. If we include in a projection equation, such as Eq. E.9, all the possible higher body RDM, $n > 2$ in our case, for a given model function ϕ_μ and use cumulant decompositions for all of them, then, in general, all the disconnected terms cancel out because of the validity of lower body equations, leaving us with connected terms and higher body cumulants. Clearly, this method will prove to be more profitable for the general mh-np case. We note that although in our h-p model spaces, all higher body Λs are of EPV type, such is not the case of a general mh-np active space. The alternative strategy introduced by us above becomes then much easier for the purpose of discerning connectivity.

Since the above two strategies are equivalent for proving the connectedness of the working equations, in our actual implementation we have used the parent projection equations like Eq. E.9. Solving Eqs. E.8 and E.9 is equivalent to solving Eqs. E.8 and E.18 and the same is true for other projection equations. We must, however, bear in mind that, although the n-body RDM elements corresponding to the EPV types are zero, the corresponding n-body Λs are necessarily not so. Hence, in order to adopt this scheme one must start with all possible RDMs, *even those of ranks beyond the number of active electrons*, in the parent projection equations. For the h-p case, the vanishing Γ_3s are actually implicitly included (though only formally so).

We also note that approximations in Λ may be made, especially for more than two active electrons. Such approximations are more valid physically than a similar truncation in the rank of Γ. An n-body Λ corresponds to an n-electron correlation contribution and hence might decay rapidly with increase in *'n'*, while an n-body Γ may be related to *'upto'* n-electron correlation and hence, a truncation in its rank cannot be related to physical considerations. In a case of more than two active electrons, the non-zero three body RDMs arise in this formulation. However, it is highly beneficial to use only up to two-body RDMs and hence, the latter scheme allows us the possibility under the approximation that we neglect three and higher body cumulants.

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Appendix 6

EOM-CC Basics

EOM-CC considers a closed shell ground state, ψ_{gr}, correlated at the CC level and aims to generate the higher energy states, ψ_k, having same or different number of electrons by a linear operator on the correlated ground state function. Notationally, we may write the parametrized wave functions as:

$$\psi_{gr} = \exp(T)\phi_0 \tag{F.1}$$

$$\psi_k = \exp(T)R_k\phi_0 \tag{F.2}$$

where,

$$R_k = Y_k^{\dagger} c_k \tag{F.3}$$

The Schrödinger equations for the two states are thus,

$$\begin{aligned} H\exp(T)\phi_0 &= E_{gr}\exp(T)\phi_0 \\ \exp(-T)H\exp(T)\phi_0 &= E_{gr}\phi_0 \\ \overline{H}\phi_0 &= E_{gr}\phi_0 \end{aligned} \tag{F.4}$$

and

$$H\exp(T)R_k\phi_0 = E_k\exp(T)R_k\phi_0 \tag{F.5}$$

Pre-multiplying Eq. (F.4) by R_k and subtracting it from Eq. (F.5), we arrive at the equation:

$$[\overline{H}, R_k]\phi_0 = \Delta E_k R_k \phi_0 \tag{F.6}$$

where,

$$\Delta E_k = E_k - E_{gr} \tag{F.7}$$

Note that, R_ks are chosen to be of excitation structure only and hence, commute with the T-operators. If R_ks and Ts were not commuting, an alternative inequivalent parametrization of ψ_k would have been,

$$\psi_k = R_k \exp(T)\phi_0 \tag{F.8}$$

Projecting with the manifold of excited functions, we get:

$$\sum_l \langle\phi_0|Y_l[\overline{H}, Y_k^\dagger]|\phi_0\rangle c_k = \sum_l \Delta E_k \langle\phi_0|Y_l Y_k^\dagger|\phi_0\rangle c_k \tag{F.9}$$

For an orthonormal set of excited functions, Eq. (F.9) reduces to Eq. (F.10):

$$\sum_l (\langle\phi_0|Y_l \overline{H} Y_k^\dagger|\phi_0\rangle - \langle\phi_0|Y_l Y_k^\dagger \overline{H}|\phi_0\rangle)c_k = \sum_l \Delta E_k \delta_{lk} c_k \tag{F.10}$$

The E_{gr} part of $\overline{H}$ cancels between the first and second terms on the LHS .

$$\sum_l (\langle\phi_0|Y_l \overline{H}_{op} Y_k^\dagger|\phi_0\rangle - \langle\phi_0|Y_l Y_k^\dagger \overline{H}_{op}|\phi_0\rangle)c_k = \Delta E_k c_k \tag{F.11}$$

In the second term on the left of Eq. (F.11), $Y_l Y_k^\dagger = \delta_{lk}$ which survives only for l=k when $\langle\phi_0|\overline{H}_{op}|\phi_0\rangle = 0$. Thus, the final equation for EOM-CC takes the form:

$$\sum_l (\langle\phi_l|\overline{H}_{op}|\phi_k\rangle c_k = \Delta E_k c_k \tag{F.12}$$

In this way all of Fock space (i.e., the space with any number of electrons) is accessible to the EOM-CC equations which amount to just a non-Hermitian matrix diagonalization. The matrix to be diagonalized is by construction non-Hermitian as $\overline{H}_{QP} = 0$ but $\overline{H}_{PQ} \neq 0$ and may sometimes give complex eigenvalues although this is quite rare. An alternative is to project with the true left eigenvectors of $\overline{H}$ which is called Λ-EOM-CC. In the latter case, both $\overline{H}_{QP} = 0$ and $\overline{H}_{PQ} = 0$.

EOM-CC treats ϕ_0 like a CC and the excited functions like a CI. It is understandable that this theory is thus only "core extensive" which means that with increasing system size, the core energy, E_{gr}, scales properly but the valence correlation introduced for the target P-space functions via the diagonalization does not. However, since the bulk of the energy comes from the core, EOM-CC is a better theory than just a CI.

The very common choices of R_ks for excited state generation are combinations of h-p and 2h-2p creation operators with respect to $|0\rangle$ taken as the vacuum and for ionization, h creation and 2h-p creation opera- tors. Except for a closed shell single determinant $|0\rangle$ reference state, the excited state energies E_k also correspond to spin broken solutions. One important virtue of the response methods is that the excitation energy, ΔE_k can be directly computed. In fact, the excited state energies, E_k, if desired, are obtained by the formula $E_k = E_g + \Delta E_k$. This is why the response methods are ideally suited for excitation or ionization energies with respect to a closed shell ground state.

Appendix 7

Sample Input Files

In this appendix we first provide the meanings of the possible keywords in the input file ***mrcc.inp*** and explain how to set up the model function definitions in the file ***modelfn.inp***. We then provide two sample input files for the three spin-free MRCC theories which can be run using this code. The keyword dependencies are also explained as completely as possible. Some keywords may appear to be redundant as the code also has some capabilities of running analytic gradients for computation of properties which is under development but we mention the keywords here for completeness. The output is written to screen and to the output file ***mrcc.out***. The output file also contains some additional information.

mrcc.inp

$mol
mol=name of molecule
nucr=nuclear repulsion energy
diphf_x,diphf_y,diphf_z=x,y and z components of the dipole moment at the SCF level

$norb
nbfn=no. of basis functions
no=number of inactive occupied
nu=number of inactive virtuals

nact=number of active orbitals
nah=number of active holes
nap=number of active particles

$modelspace
nvac= model space dimension
ne=number of active electrons

$state
istate=targeted state (as per GUGA-MCSCF ordering) for state specific calculations
spin=spin multiplicity of state, spin=1 for singlet, 2 for doublet, 3 for triplet, etc.

$filenames
vfile=Name of 2e integral file (generally vfile=DASORT for UGA-SUMRCC/UGA-QFMRCC/UGA-SSMRCC+GAMESS)
fmat=Name of 1e integral file (generally fmat=FOCKMAT for UGA-SUMRCC/UGA-QFMRCC+GAMESS and fmat=FCORE for UGA-SSMRCC+GAMESS)
dipolx,dipoly,dipolz=Name of dipole integral file (generally dipx,dipy,dipz)
vfile,fmat,dipolx,dipoly,dipolz are not required if in $flags package='dirac' or 'london'
t1file,t2file= Name of file for writing converged t and s amplitudes

$flags
sector = 1 for n-hole valence sector
= 2 for n-particle valence sector
= 3 for 1h-1p valence sector
MCSCF=.true. if orbitals are MCSCF orbitals; CAS matrix is recomputed.
LIN=.true. if only linearly independent T operators are desired. At present implemented for 1h-1p and 2p triplet only
LCCD=.true. if only linear CCD is desired
OR
LCCSD=.true. if only linear CCSD is desired
OR
CCD=.true. if non-linear CCD is desired
OR
CCSD=.true. if full non-linear CCSD is desired
package='gamess' or 'dirac' or 'london', the name of the package supplying integral files
PROP=.true. if property calculations are required
AT=.false. if auto_tensor is not desired for tensor contractions (currently cannot be

used)
QF=.true. for UGA-QFMRCC
OR
SS=.true. for UGA-SSMRCC
OR
SRCC=.true. for SRCC
UGA-SUMRCC is the default
OUT_OF_CORE=.true. if out of core storage for VPPPP integrals is desired

$iteration
nitmax_T= max no. of iterations for T_eq
iconv_T=10E-iconv is the convergence criteria for T
nitmax_L=max no. of iterations for T_eq
iconv_L=10E-iconv is the convergence criteria for λ

$thresholds
thrs=threshold value for writing converged t and s amplitudes
tlrnc=threshold value for setting very small t amplitudes to zero
iter_freeze=number of initial iterations for which the t amplitudes of model functions with coefficients less than 10^{-3} will be kept frozen at the perturbative value

$shifts
sh_T,sh_L=Denominator shift to aid in convergence;It is a tunable parameter for T and λ respectively
fact= fact is multiplied to residue before increment of T and L is calculated
denom_shift=.false. if only orbital energy differences are desired as denominator for updating t amplitudes

$diisgrp
diis=1,2,3,...,nvac if DIIS is desired for all model fns. Put 0 for those model fns where DIIS is not desired
diis_solver= 1 for non-overlapping scheme; requires ndiis and nskip
= 2 for cumulative scheme; requires diismin and diismax
ndiis=No. of past iteration vectors desired in the iterative subspace
nskip=No. of iterations after which DIIS will be done periodically
diismin=minimum no. of vectors to be kept in the iterative subspace
diismax=maximum no. of vectors to be kept in the iterative subspace

modelfn.inp

Three lines are required for each model function CSF. The CSFs are identified by the occupancies of the active orbitals. CSFs with same occupancy but different spin-coupling schemes must be repeated in the input. The lines are unformatted and have the following meanings:

First line : ndoc nopn_h nopn_p nvirt
Second line : Orbital indices of occupied/partly occupied orbitals in the order doubly occupied followed by singly occupied
Third line : Orbital indices of unoccupied/partly unoccupied orbitals in the order singly occupied followed by unoccupied

ndoc, nopn_h, nopn_p and nvirt are the number of doubly occupied, singly occupied hole, singly occupied particle and vacant orbitals in the model function respectively.

Defaults

PROP=.false.
LCCD=.false.
LCCSD=.false.
CCD=.false.
CCSD=.true.
AT=.true.
QF=.false.
SS=.false.
OUT_OF_CORE=.false.
RESTART=.false.
nrestart=0
denom_shift=.true.
nvac=0
diis_solver=2

UGA-SUMRCC for ionizations from HOMO and HOMO-1 of H_2O in cc-pVDZ basis using integrals from GAMESS

mrcc.inp

```
&MOL molecule=’H2O’ nucr=9.0092847301 diphf_x=0.0 diphf_y=0.0 diphf_z=0.0 &END
&STATE istate=1 spin=2 &END
&FLAGS MCSCF=.F. LIN=.F. sector=1 CCSD=.T. package=’gamess’ QF=.F. AT=.T.
&END
&NORB nbfn=24 no=3 nu=19 nact=2 nah=2 nap=0 &END
&MODELSPACE ne=3 nvac=2 &END
&ITERATION iconv_T=8 iconv_L=8 nitmax_T=100 nitmax_L=100 &END
&SHIFTS fact=1.0d0 sh_T=0.0d0 sh_L=0.0d0 &END
&THRESHOLDS thrs=10E-2 &END
&DIISGRP diis(1)=1,2 diismin=3 diismax=5 &END
&FILENAMES vfile=’DASORT’ fmat=’FOCKMAT’ t1file=’T1.DAT’ t2file=’T2.DAT
’ dipolx=’DIPX’ dipoly=’DIPY’ dipolz=’DIPZ’ &END
```

modelfn.inp

```
1 1 0 0
4 5
5
1 1 0 0
5 4
4
```

UGA-SSMRCC for $^1\Sigma$ ground state of LiH using (2,2) CAS in cc-pVDZ basis using integrals from GAMESS

mrcc.inp

```
&MOL molecule=’LiH’ nucr=0.9922073423 diphf_x=0.0 diphf_y=0.0 diphf_z=0.0 &END
&STATE istate=1 spin=1 &END
&FLAGS MCSCF=.T. LIN=.F. sector=2 CCSD=.T. package=’gamess’ AT=.T. SS=.T.
&END
&NORB nbfn=19 no=1 nu=16 nact=2 nah=0 nap=2 &END
&MODELSPACE nvac=3 ne=2 &END
&ITERATION iconv_T=8 iconv_L=8 nitmax_T=100 nitmax_L=100 &END
&SHIFTS fact=1.0d0 sh_T=0.0d0 sh_L=0.0d0 &END
```

```
&THRESHOLDS thrs=10E-3 tlrnc=10E-4 iter_freeze=0 &END
&DIISGRP diis(1)=1,2,3 diismin=2 diismax=4 &END
&FILENAMES vfile=’DASORT’ fmat=’FCORE’ t1file=’T1.DAT’ t2file=’T2.DAT ’
dipolx=’DIPX’ dipoly=’DIPY’ dipolz=’DIPZ’ &END
```

modelfn.inp

```
1 0 0 1
2
3
0 1 1 0
2 3
2 3
1 0 0 1
3
2
```

LIST OF PUBLICATIONS

(1) Recent advances in spin-free state-specific and state-universal multi-reference coupled cluster formalisms: A unitary group adapted approach
R. Maitra, D. Sinha, S. Sen, A. Shee and D. Mukherjee in *Theory and Applications in Computational Chemistry. The First Decade of the Second Millenium*; ed. E. Clementi, AIP Conf. Proc. **1456**, 81 (2012).

(2) Formulation and implementation of a unitary group adapted state universal multi-reference coupled cluster (UGA-SUMRCC) theory: Excited and ionized state energies
S. Sen, A. Shee and D. Mukherjee, *J. Chem. Phys.* **137**, 074104 (2012).

(3) Exploration of various aspects of UGA-SUMRCC: Size extensivity, possible use of sufficiency conditions, and an extension for direct determination of energy differences
A. Shee, S. Sen and D. Mukherjee, *J. Chem. Theory Comput.* **9**, 2573 (2013).

(4) A study of the ionisation and excitation energies of core electrons using a unitary group adapted state universal approach
S. Sen, A. Shee and D. Mukherjee, *Mol. Phys.* **111**, 2625 (2013).

(5) Aspects of Size-Extensivity in Unitary Group Adapted Multi-Reference Coupled Cluster Theories:The Role of Cumulant Decomposition of Spin-free Reduced Density Matrices
R. Maitra, D. Sinha, S. Sen and D. Mukherjee, *Theor. Chem. Acc.* **133**, 1522 (2014)

(6) Unitary group adapted state specific multireference perturbation theory: Formulation and pilot applications
A. Sen, S. Sen, P. K. Samanta and D. Mukherjee, *J. Comput. Chem.* **36**, 670 (2015)

(7) Analytic gradients for unitary group adapted state universal multi-reference coupled cluster (UGA-SUMRCC) theory
S. Sen and D. Mukherjee, *Work in progress.*

(8) Scalar relativistic effects on ionization of core electrons: A study using Unitary Group Adapted Open-Shell Coupled Cluster (UGA-OSCC) theory

S. Sen, A. Shee and D. Mukherjee, *Manuscript under preparation*

(9) Scalar relativistic effects on excitation of core electrons: Use of Intrinsic Atomic Orbitals for Model Space Selection in Conjunction with Unitary Group Adapted Open-Shell Coupled Cluster (UGA-OSCC) theory
Work in Progress

(10) Aspects of Implementational Improvements to Spin-free Multi-Reference Coupled Cluster theories
Work in Progress