Studies of Molecular Properties using State-Universal Multi-Reference Coupled-Cluster Approach

Thesis submitted to the
University of Pune
for the degree of

Doctor of Philosophy
in
Chemistry

by

K. R. Shamasundar

Physical Chemistry Division
National Chemical Laboratory
Pune - 411 008, India.

APRIL 2004

CERTIFICATE

This is to certify that the work presented in this thesis entitled, "**Studies of Molecular Properties using State-Universal Multi-Reference Coupled-Cluster Approach**" by **K. R. Shamasundar**, for the degree of Doctor of Philosophy, was carried out by the candidate under my supervision in the Physical Chemistry Division, National Chemical Laboratory, Pune, India. Any material that has been obtained from other sources has been duly acknowledged in the thesis.

Date: Dr. Sourav Pal

Place: (Research Guide)

Acknowledgements

This is indeed the right place to place a bouque of my sincere and heartfelt gratitude to my thesis supervisor Dr. Sourav Pal. I am indebted to him for his constant encouragement and invaluable guidance during the course of this research work. The atmosphere of academic freedom I enjoyed in his presence was really helpful for me to courageously go down the untrodden paths in quantum chemistry. It is my pleasure to keep on records the deep respect and appreciation I have towards him.

I take this opportunity to thank all my labmates and colleagues for the pleasurable company. Special thanks go to my seniors Ajitha, Nayana, and of course to the *most-polite-lady* Sailaja for their invaluable help. My association with Chandra has been a fountain full of wonderful memories. I thank him and Maneesha for their care and timely help. My juniors Sharan, Prashant, Sophy, Sajeev, Subashini, and Akhilesh also deserve a special appreciation for the cheerful moments we have all had together.

Thanks to all my Kannada friends, I have had a wonderful time here with them during my initial years. I specially thank Prasad Pujar, Bennur, M. P. Kulkarni, R. V. Naik, and Arun Gunari. Special thanks should go to my Indian classical music circle friends, Chaitanya, Shruti, Aniruddh, Parag, Meghana, Saniya and others at Indian classical music circle. I fondly remember my didi Prachi for her love and affection, and her guidance. I also thank Dr. Madhav Ghate for his suggestions and constant encouragement.

I express my deep appreciation towards some of my close friends, Rao, Parag, Revaiah, Govind, Chiru. I cherish all the wonderful moments I have had with them. I can not end this note without thanking my friends Buffy, Neha, Bhupesh, Sonum, Deepa, Farah, Faru and Rani, and Divya for their friendly and cheerful company. Of course,

words are not enough to express my gratitude to my parents and sisters for their love and affection, and being there with me.

Finally, I thank the director of National Chemical Laboratory, for permitting to take up my research fellowship at the Physical Chemistry Division. I also thank the EMR division of CSIR, New Delhi, for research fellowship

Date:

Place: (K. R. Shamasundar)

.

Table of Contents

Chapter I:

Chapter II:

Chapter III:

Chapter VI:

Attempts towards formulation of a size-extensive stationary state-selective MRCC theory 199

Abstract

This thesis is mainly concerned with development of theoretical and computational techniques for efficient computation of atomic and molecular properties in quantum chemistry using multi-reference coupled-cluster (MRCC) theories. The necessity and importance of multi-reference theories for proper treatment of electron correlation in low-lying quasi-degenerate states of atoms and molecules has been well recognized. Among a host of multi-reference theories that have been developed so far, MRCC theories, in one form or the other, stand out due to several important theoretical features they possess.[1-2]

The single-reference coupled-cluster (SRCC) theory is one of the most accurate and widely used electronic structure methods for studying ground state structure, properties, spectroscopy and dynamics of closed-shell molecules around equilibrium geometry[3-5]. Apart from a high-level treatment of electron-correlation, the most attractive feature of SRCC is its in-built size-extensivity and size-consistency property.[1-2,4] It is the failure of SRCC to properly describe electron correlation in general quasi-degenerate situations such as potential energy surfaces at bond-breaking/bond-making regions, open-shell atomic states and low-lying excited states of molecules, that has led to MRCC theories.[1-2] Among the MRCC theories formulated so far, the ones based on effective Hamiltonian defined over a small model space are theoretically well-understood. One important feature of this class of MRCC theories is that the energies and wave-functions of a manifold of strongly interacting quasi-degenerate states approximately described by the chosen model space are simultaneously obtained by constructing and diagonalizing an effective Hamiltonian within the model space.[6-7] Two effective Hamiltonian based

MRCC theories have emerged as standard, namely, the valence-universal MRCC (VUMRCC) and the state-universal MRCC (SUMRCC).[1-2,8,9] Both differ in the nature of ansatz they use for the wave-operator, and hence are suitable for different types of situations.

One disadvantage suffered by SRCC in its earlier days when its routine applications were initiated in chemistry was the difficulty in analytic computation of molecular energy gradients and hessians, molecular dipole moments and higher-order properties such as polarizability. The response approach for SRCC was formulated by Monkhorst[10] to enable analytic computation of such properties. The SRCC was originally formulated in a non-stationary framework,[3] and due to this it did not have the simplicities introduced by the generalized Hellmann-Feynman theorem and the $(2n+1)$-rule.[11] As a result, the expression for a first-order property in SRCC depended explicitly on first-derivatives of cluster amplitudes with respect to the external perturbation, and it seemed to be necessary to calculate these cluster amplitude derivatives for all modes of perturbation.[10,12] For first-order properties, this apparent impediment was overcome by Bartlett and coworkers[13] using the idea of algebraic Z-vector method introduced by Handy and Schaefer[14] in their analysis of analytic derivatives for the configuration interaction method. This and the subsequent developments by Bartlett and coworkers[15] substantially facilitated efficient implementation of molecular energy gradients for SRCC, and significantly contributed to its success in quantum chemistry.[5]

Although pursued by Bartlett and coworkers,[16] Z-vector type of approach turned out be tedious for higher-order properties such as hessians and polarizabilities. On the other hand, a conceptually different approach known as constrained variation approach, proposed by Jorgensen and coworkers,[17] turned out to be useful. This approach involved

recasting of standard SRCC theory in a stationary framework by introducing an extra set of de-excitation amplitudes. It was shown that this method includes the Z-vector method as a zeroth-order result and transparently extends its benefits to higher-order properties.[17]

With MRCC theories well established to describe general quasi-degenerate situations, studies of molecular properties using these theories are being pursued. A response approach suitable for effective Hamiltonian MRCC theories has been formulated by Pal.[18] Its applications for the first-order molecular properties have been carried out in recent years to calculate dipole moments of open shell radicals and excited states of several molecules.[19] The above developments do not include the Z-vector method. A constrained variation approach along the lines of Jorgensen and coworkers[17] has been used by Szalay[20] for a theoretical estimate of the relative cost of MRCC first-order property calculations as compared to SRCC calculations.

An extension of various theoretical and computational developments in SRCC response approach which enabled it to be suitable for routine use has not been studied in detail for MRCC methods. A systematic study of the concepts and various issues involved in such an extension forms the subject matter of this thesis. These developments are expected to initiate routine applications of MRCC methods to study molecular properties of quasi-degenerate systems. The present thesis is organized as follows.

The first chapter is a general introduction leading to the subject matter of the thesis. Here, a brief overview of some of the basic concepts and developments in quantum chemistry is presented. Different quantum chemical methods used for treatment of electron correlation are briefly described. Quasi-degenerate situations and their multi-reference treatments are highlighted. The response approach for computation of various atomic and molecular properties within quantum chemistry is discussed. Important developments for efficient evaluation of atomic and molecular properties using electron correlation methods, especially the SRCC and MRCC methods, are summarized. Finally, the objectives and scope of the thesis are defined.

The second chapter is concerned with extension of the algebraic Z-vector method for the SUMRCC theory. Towards this end, with a brief description of developments in SUMRCC theory, the time-independent response approach is applied to obtain a theoretical framework for computation of molecular properties. An analysis of resulting first-order response equations reveals two distinct routes to extend SRCC Z-vector method for SUMRCC theory. Extension of other important concepts and ideas emerged during the development of efficient SRCC gradient methods, is also discussed

In the third chapter, a state-dependent constrained variation approach for SUMRCC theory is proposed after a brief discussion on its use in SRCC. The proposed functional includes state-dependent Z-vector method of the second chapter as a zeroth-order result. Certain degree of freedom in choice of constrained variation functional is observed. This enables comparison of the proposed functional with the functional used by Szalay.[20] The formalism is then applied, in conjunction with $(2n+1)$ and $(2n+2)$ rules, to obtain generic expressions for up to third-order molecular properties in SUMRCC theory. This highlights the advantages of state-dependent constrained variation approach for higher-order molecular properties.

The fourth chapter reports a pilot application of complete model space based SUMRCC for computation of molecular properties using both finite-difference and analytic methods. The dipole moment surfaces of ground and three low-lying excited states of HF molecule at different inter-nuclear distances are obtained within double-zeta basis set using a complete model space consisting of highest occupied and lowest unoccupied molecular orbitals of proper symmetry. Behaviour of dipole moment surfaces for ionic as well open-shell dissociation channels is analyzed in terms of nature of dominating model space configurations. Attempts to progress to higher basis sets and to other simple hetero-nuclear diatomic molecules result in convergence difficulties due to poorer description of a state. Nature of this state is discussed and available approaches to solve convergence problems are outlined.

The fifth chapter mainly deals with the use of constrained variation procedure to VUMRCC theories, thus extending the scope of application of MRCC response approach to higher-order properties of ionized, electron-attached, excited and several other states. In this context, a generalization constrained variation procedure to general incomplete model spaces is made. This is an essential development for higher-valence sectors of VUMRCC theory. The constrained variation procedure can similarly be generalized to incomplete model space based SUMRCC theories. In the fifth chapter, a brief review of essential elements of incomplete model space based MRCC theories is first presented. An analysis of structure of such MRCC theories reveals that the method used for obtaining Lagrange multiplier equations is somewhat different from the earlier approaches. Essential simplifications arising when effective Hamiltonian definition becomes explicit are discussed. The method is then applied to generate explicit generic expressions for up to third-order response properties in VUMRCC theory using one valence-hole, one valence-particle, and the one valence hole-particle Fock-space sector model spaces. Specific diagrammatic expressions for zeroth-order Lagrange multiplier equations for each of these sectors are also presented.

The last chapter is an exploratory one in which we describe our incomplete attempts towards formulating a size-extensive stationary state-selective MRCC theory. A brief discussion on currently available single-reference coupled-cluster ansatz based stationary theories is carried out, highlighting various theoretical issues associated with them.[17, 21] The relation between constrained variation approach for the standard SRCC and extended coupled-cluster (ECC) theory is outlined.[21-22] When combined with the results of multi-reference constrained variation approach, this points towards a possible multi-reference generalization of ECC (MR-ECC) theory, as a size-extensive stationary state-specific MRCC theory. We identify a possible paradigm within which a possible MR-ECC formulation can be searched. This is followed by a discussion on recent state-selective or single-root theories, pointing out their basic features or ingredients. Based on constrained variation approach for SUMRCC theory and for a non-stationary state-selective MRCC theory recently proposed by Mukherjee and coworkers,[23] two stationary state-selective MRCC theories are derived. The structure of these theories is discussed by analyzing their working equations. The possible theoretical problems, which need to be solved to reach a solution within the proposed paradigm, are outlined.

References

1. D. Mukherjee, Pal, S. Adv. Quant. Chem. **20**, 291 (1989)

2. J. Paldus, in Methods of Computational Molecular Physics, edited by S. Wilson, and G. H. F. Dierckson (NATO ASI Series B, Plenum, New York, 1992)

3. J. Cizek. Adv. Quant. Chem. **14**, 35 (1969)

4. (a) R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981) (b) R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989)

5. R. J. Bartlett in Modern electronic structure theory, edited by D. R. Yarkony (World Scientific, Singapore, 1995) p1047

6. P. Durand, and J. P. Malrieu, Adv. Chem. Phys. **67**, 321 (1987)

7. V. Hurtubise, and K. F. Freed, Adv. Chem. Phys. **83**, 465 (1993)

8. D. Mukherjee, and I. Lindgren, Phys. Rep. **151**, 93 (1987)

9. B. Jezioroski, and H. J. Monkhorst, Phys. Rev. **A24**, 1668 (1982)

10. H. J. Monkhorst, Int. J. Quant. Chem. **S11**, 421 (1977)

11. S. T. Epstein, *The Variation Principle in Quantum Chemistry*, (Academic, New York, 1974)

12. P. Jorgensen, and J. Simons, *Second quantization based methods in quantum chemistry*, (Academic, New York, 1981)

13. R. J. Bartlett, in *Geometrical Derivatives of Energy Surface and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht,1986), p35

14. N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984)

15. (a) L. Adamowicz, W. D. Laidig, and R. J. Bartlett, Int. J. Quant. Chem. **S18**, 245 (1984) (b) G. Fitzgerald, R. J. Harrison, and R. J. Bartlett, J. Chem. Phys. **85**, 5143 (1986) (c) E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989)

16. E. A. Salter and R. J. Bartlett, J. Chem. Phys. **90**, 1767 (1989)

17. (a) T. Helgaker and P. Jorgensen, Adv. Quant. Chem. **19**, 183 (1988) (b) H. Koch, H. J. A. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria, H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990)

18. (a) S. Pal, Phys. Rev. **A39**, 39 (1989) (b) S. Pal, Int. J. Quant. Chem. **41**, 443 (1992)

19. (a) D. Ajitha and S. Pal, Phys. Rev. **A56**, 2658 (1997) (b) D. Ajitha, N. Vaval, and S. Pal, J. Chem. Phys. **110**, 2316 (1999) (c) D. Ajitha and S. Pal, Chem. Phys. Lett. **309**, 457 (1999) (d) ibid, J. Chem. Phys. **114**, 3380 (2001) (e) N. Vaval and S. Pal, Chem. Phys. Lett. **300**, 125 (1999)

20. P. G. Szalay, Int. J. Quant. Chem. **55**, 151 (1994)
21. (a) S. Pal, Theor. Chim. Acta **62**, 523 (1983) (b) N. Vaval, K. B. Ghose and S. Pal, J. Chem. Phys. **101**, 4914 (c) N. Vaval, and S. Pal, Phys. Rev. **A54**, 250 (1996) (d) N. Vaval, A. B. Kumar, and S. Pal, Int. J. Mol. Sci. **2**, 89 (2001) (e) N. Vaval, Chem. Phys. Lett. **318**, 168 (2000) (f) P. U. Manohar, N. Vaval, and S. Pal, Chem. Phys. Lett. **387**, 442 (2004)
22. J. Arponen, Ann. Phys. 151, 311 (1983)
23. U. S. Mahapatra, B. Datta, B. Bandopadhyay, and D. Mukherjee, Adv. Quant. Chem. **30**, 163 (1998)

List of Publications

1. K. R. Shamasundar, and S. Pal, *Development of an efficient linear response approach to the Hilbert space multi-reference coupled-cluster theory*, J. Chem. Phys. **114**, 1981 (2001); **115**, 1979 (E) (2001)
2. K. R. Shamasundar, and S. Pal, *Higher Energy Derivatives in Hilbert Space Multi-Reference Coupled Cluster Theory : A Constrained Variational Approach*, Int. J. Mol. Sci. **3**, 710 (2002)
3. K. R. Shamasundar, S. Asokan, and S. Pal, *A constrained variational approach for energy derivatives in Fock-space multireference coupled-cluster theory*, J. Chem. Phys. **120**, 6481 (2004)

Chapter I

General introduction and scope of the thesis

I.1 Introduction

Quantum chemistry is one of the most successful branches resulting from application of quantum physics to problems in chemistry.[1-3] Significant theoretical and computational developments have taken place in quantum chemistry in the past few decades.[4-12] Importance of proper treatment of electron correlation effects in atoms and molecules necessitated to look beyond simple mean-field approaches such as Hartree-Fock (HF) method. Studies of electron correlation effects in ground state of closed-shell systems resulted in a variety of methods such as the configuration interaction (CI) method,[13-15] the many-body perturbation theory (MBPT),[16-19] and the coupled-cluster (CC) method.[19-25] Size-extensivity and size-consistency criteria have also been a guiding factor in choosing methods for practical applications. Since these methods are mainly capable of treating electron correlation effects in systems with a single dominating configuration, they are collectively known as single-reference (SR) methods.

The success of SR methods in explaining structure and properties of ground state of closed-shell atomic and molecular systems spawned two different lines of research beginning around the end of seventies. The first line was to suitably extend SR methods for treatment of electron correlation effects in quasi-degenerate systems. These developments resulted in multi-reference (MR) methods capable of describing strongly interacting ground and close-lying excited states, a situation known as quasi-degeneracy. Some important MR methods are multi-reference configuration interaction (MRCI),[26] multi-reference perturbation theory (MRPT),[27-29] multi-reference coupled-cluster

(MRCC) theory.[25,30,] Due to many theoretical and computational difficulties associated with them, MR methods are not as popular as their SR counterparts. In particular, they do not offer a convenient block-box type of solution. They continue to be developed even today and a clear method of choice has still not emerged. Each MR method has its own window of applicability as well as limitations.

The second line of research has been the development of efficient theoretical and computational techniques to study molecular energy gradients and hessians, and various atomic and molecular properties, using SR electron correlation methods.[31-35] Although methods to compute properties such as molecular energy gradients and hessians were available much earlier for HF and HF-like methods,[36] they were not particularly suitable for electron correlation methods. This is especially relevant for non-stationary methods such as MBPT and CC, where the generalized Hellmann-Feynman theorem and the $(2n+1)$-rules are not applicable.[37] For first-order properties, the Z-vector method introduced by Handy and Schaefer[38] had been very useful to avoid direct expensive computation of perturbation-dependent first derivatives of non-variationally determined electron correlation parameters.[38-41] Introduction of effective density matrices has also been another important development.[42] There have been further studies to extend the benefits of these techniques for higher-order properties.[41,43-44] In all these developments, the analytic response approach[41,45] has made it possible to bring seemingly different kind of properties under a single unifying theme. In this approach, molecular energy gradients and hessians required for treatment of potential energy surfaces can be studied and computed with the same techniques used for computing molecular electric dipole moments and polarizabilities. Time-dependent response approach covers even wider range of properties such as excitation energies and frequency dependent polarizabilities.[45]

All these developments have certainly contributed in part to the success of SR methods, especially non-stationary ones such as MBPT and CC, and made their routine application feasible.

For MR methods, again for non-stationary variants such as MRPT and MRCC, similar developments have been somewhat late in coming. General analytic response based approach for effective Hamiltonian based MRCC methods has been formulated[46] and applied to compute dipole moments of open-shell radicals and excited states of several molecules.[47] A time-dependent analytic response approach has also been recently formulated to enable computation of frequency dependent properties using MRCC methods.[48] A constrained variation approach along the lines of Helgaker and Jorgensen[41] has been used by Szalay for estimating the relative cost of a MRCC first-order properties.[49] Implementation and application of analytic gradient methods for different variants of MRPT have appeared recently.[50-52] Similarly, analytical gradients for other SR based methods closely related to MRCC have also appeared in recent times.[49,53-54]

However, developments to obtain efficient theoretical and computational techniques parallel to the ones used in SR methods has not been pursued in detail for effective Hamiltonian based MRCC methods. Some recent notable works in this direction include an attempt by Ajitha and Pal[55] to extend the Z-vector method for the valence-universal MRCC method, and the above mentioned study by Szalay.[49]

In the present thesis, we propose to pursue some theoretical and computational developments in this direction. We begin with the state-universal MRCC method, and touch upon the valence-universal variant towards the end. Our intention is to suitably extend the algebraic Z-vector method for state-universal MRCC theory, and study its relation with the constrained variation approach for MRCC theories. The advantage of these results for computation of higher-order properties using MRCC theories is illustrated. Pilot applications of the developed formalism to compute ground and low-lying excited state dipole moment surfaces of small hereto-nuclear diatomic molecules are also planned. Our motivation for research in this direction mainly comes from two factors. First and foremost is that these developments prove valuable for efficient computation of atomic and molecular properties as well as for investigation of potential energy surfaces using MRCC theories. In addition, as it happened in case of SR methods, it may possibly give some ideas for formulation of stationary MRCC theories.

To place the relevance of the proposed work in a perspective, in this chapter, we present an overview of some of the basic concepts and developments in quantum chemistry. Description of different quantum chemical methods is given by connecting them in a thematic sequence based on electron correlation, size-extensivity, quasi-degeneracy and non-dynamical correlation. Developments in effective Hamiltonian based MRCC theories are discussed in some detail. The response approach as a framework for computation of atomic and molecular properties is presented. This is followed by analysis of significant advances which have made efficient evaluation of atomic and molecular properties using non-stationary electron correlation methods such as CC theory, possible. Finally, objectives and scope of the thesis are summarized.

I.2 Quantum mechanical description of atoms and molecules

Atoms and molecules are quantum bound states formed by a delicate balance of attractive and repulsive electromagnetic interactions among a pool of electrons and nuclei in motion. Their quantum mechanical description involves solution of corresponding time-independent Schrödinger equation to determine the system wave-function Ψ.[1-2]

$$\hat{H}\,|\Psi\rangle = \mathcal{E}\,|\Psi\rangle \tag{1.1}$$

Here, $\hat{H}$ is the Hamiltonian operator for the total energy of the system. It includes kinetic energy of constituent particles and potential energy resulting from various interactions among them. Although such a complicated system can have many possible interactions of varying strengths, consideration of dominating electrostatic interactions is sufficient for understanding structure and stability of atoms and molecules. Within this approximation, the Hamiltonian for a molecule with M nuclei and N electrons can be written as follows.[2]

$$\begin{aligned}\hat{H} = &-\sum_{A=1}^{M}\tfrac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\tfrac{1}{2}\nabla_i^2 - \sum_{i=1,A=1}^{i=N,A=M}\frac{Z_A}{\|\vec{r}_i-\vec{R}_A\|} \\ &+\sum_{i,j,i<j}^{N}\frac{1}{\|\vec{r}_i-\vec{r}_j\|} + \sum_{A,B,A<B}^{M}\frac{Z_A Z_B}{\|\vec{R}_A-\vec{R}_B\|}\end{aligned} \tag{1.2}$$

Here, $\vec{R}_A$ and $\vec{r}_i$ are the spatial coordinates of A-th nuclei and i-th electron respectively. The first two terms in Eq (1.2) describe the total kinetic energy of nuclei and electrons respectively. The next term describes individual electrostatic attraction between nuclei and electrons, and the last two terms respectively describe electrostatic repulsion amongst electrons and nuclei. The system wave-function Ψ is a complicated function of spatial and spin coordinates of electrons and spatial coordinates of nuclei. Denoting combined space-spin coordinate of i-th electron by $\vec{x}_i = (\vec{r}_i, \xi_i)$, the electron-nuclear system wave-function Ψ is written as $\Psi(\vec{R}_1,\ldots,\vec{R}_M,\vec{x}_1,\ldots,\vec{x}_N)$. Solution of eigenvalue problem Eq (1.1) yields stationary state energies and wave-functions. In absence of any external perturbation, atoms and molecules are assumed to be one of these stationary states, usually the stable ground state.

It is well known that, even for small systems, solution of Eq (1.1) is intractable and further approximations are needed. One important approximation which practically pervades whole of quantum chemistry is the so-called frozen-nuclei Born-Oppenheimer (BO) approximation.[2,56-57] It is based on the fact that nuclei are much heavier compared to electrons, and as a first approximation their motion can be neglected. In other words, they can be considered as frozen during electronic motion. This is essentially equivalent to dropping the first term of Eq (2.1), and leads to following simplified electronic Hamiltonian, $\hat{H}_{el}$.

$$\hat{H}_{el} = \sum_{i=1}^{N} \hat{h}(\vec{r}_i) + \sum_{i,j,i<j}^{N} \hat{g}(\| \vec{r}_i - \vec{r}_j \|) \tag{1.3}$$

$$\hat{h}(\vec{r}_i) = -\tfrac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{\| \vec{r}_i - \vec{R}_A \|} \quad \text{and} \quad \hat{g}(\| \vec{r}_i - \vec{r}_j \|) = \frac{1}{\| \vec{r}_i - \vec{r}_j \|} \tag{1.4}$$

Since the first term in Eq (1.3) refers to coordinates of individual electrons at a time, it is referred to as one-electron (or one-body or one-particle) operator. Similarly, the second term is referred to as two-electron (or two-body or two-particle) operator. The operator $\hat{h}(\vec{r})$, also referred to as core operator, represents the Hamiltonian of an individual electron at the given nuclear configuration without considering inter-electron repulsion terms. The nuclear repulsion term has not been included in Eq (1.3) as it can be considered as a constant at a fixed molecular geometry. Solution of Eq (1.1) at a fixed nuclear configuration $(\vec{R}_1, \vec{R}_2 \ldots, \vec{R}_M)$ with the above electronic Hamiltonian Eq (1.3) yields wave-functions $\Psi_{el}(\vec{x}_1, \ldots, \vec{x}_N; \vec{R}_1, \ldots, \vec{R}_M)$ for different electronic states with corresponding electronic energies $E_{el}(\vec{R}_1, \ldots, \vec{R}_M)$. Addition of nuclear repulsion terms to electronic energy provides an effective potential energy surface (PES) $V_{eff}(\vec{R}_1, \ldots, \vec{R}_M)$ on which nuclear motion can be considered.[2,57] In principle, two such PES resulting from different electronic states may interact through the residual nuclear kinetic energy terms. However, such an interaction is negligible when nuclear motion around a region of PES energetically well separated from other PES is considered. This usually happens for ground states of closed-shell and closed-shell like molecules around their equilibrium geometry, and even in many excited states. This treatment leads to complete separation of nuclear degrees of motion such as vibrations and rotations from the electronic motion. Even when interaction between two different PES is not negligible, it can be computed in terms of these electronic wave-functions.

BO approximation is of central importance in chemistry in general, and quantum chemistry in particular. It simplifies the complicated problem involving many nuclei and electrons to an at least tractable many-electron problem at a fixed geometry. By enabling to introduce the concept of PES, it serves to bring back familiar chemist's picture of molecules as a formation with chemical bonds in between constituent atoms, and of chemical reactions as occurring on an energy landscape.

I.3 Brief description of methods in quantum chemistry

In quantum chemistry, one is concerned with finding approximate solutions of many-electron eigenvalue problem (or its equivalent formulations) at some fixed nuclear geometry to obtain energies and wave-functions of ground and low-lying excited states of atoms and molecules. Different quantum chemical methods result from different approaches to solve this many-electron problem by employing varying levels of approximations.

Methods of quantum chemistry may be classified based on several criteria. A simple classification is into semi-empirical and ab-initio methods. However, a theoretically convenient and useful criterion is whether the method is based on wave-function or (reduced) density matrix or the simple one electron density. In the following subsections, we discuss different wave-function based methods.

I.3.1 Structure of many-electron wave-function

A many-electron wave-function $\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$ is a complicated function of coordinates of electrons. Collection of all such functions form a linear vector space referred to as N-particle Hilbert space.[1-2] The function $\Psi^*\Psi$ describes the probability density of finding simultaneously, first electron at x_1, second electron at x_2 and so on. Since electrons are indistinguishable, probability density must be invariant to any arbitrary permutation of electron coordinates. This fundamental permutation symmetry requirement on many-particle wave-functions describing identical particles leads to only two allowed possibilities, namely completely symmetric and completely anti-symmetric. It is well known that electrons, being fermions with half integral spin, obey the anti-symmetry principle. Consequently, a many-electron wavefunction is fully anti-symmetric with respect to the interchange of coordinates any two electrons.

$$\Psi(\vec{x}_1, \ldots, \vec{x}_i, \ldots, \vec{x}_j, \ldots, \vec{x}_N) = -\Psi(\vec{x}_1, \ldots, \vec{x}_j, \ldots, \vec{x}_i, \ldots, \vec{x}_N) \qquad (1.5)$$

In other words, all valid many-electron wave-functions belong to the anti-symmetric subspace of the N-electron Hilbert space.[2] It is known that such an N-electron anti-symmetric wave-function can be expanded as a linear combination of complete set of known N-electron anti-symmetric functions. Although various ways to expand an anti-symmetric wave-function are available, ubiquitous in quantum chemistry is the expansion in terms of Slater determinants $\{\Phi_I, \forall I\}$ built from a complete set of one-electron basis functions $\{\chi_i(x)\ \forall i = 1, \ldots, \infty\}$ known as spin-orbitals.[2]

$$\begin{aligned}\Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) &= \sum_{I=1}^{\infty} C_I \Phi_I(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) \\ \Phi_I(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) &= \tfrac{1}{\sqrt{N!}} \| \chi_i(\vec{x}_1),\chi_j(\vec{x}_2),\ldots,\chi_k(\vec{x}_N) \| \end{aligned} \tag{1.6}$$

Slater determinants are not only a natural way to enforce the anti-symmetry principle, but are also helpful in introducing the concept of atomic and molecular electronic configuration. Normally, spin-orbitals are constructed to be eigenfunctions $\chi_i(x)$ of an one-electron Hamiltonian $\hat{h}(x)$ with corresponding eigen energy e_i, referred to as orbital energies. An N-electron configuration is defined to be an approximate N-electron state built by specifying a set of N orbitals each of them occupied by an electron. Such a configuration can be mathematically represented by the corresponding Slater determinant with occupied spin-orbitals in its columns. Therefore, the physical content of Eq (1.6) is that the exact N-electron state satisfying electronic Schrödinger equation is a combination of different N-electron configurations obtained by distributing electrons in different spin-orbitals. Importance or weight of a configuration Φ_I in a specific state is indicated by the magnitude of its combining coefficient C_I.

Another feature of a many-electron wave-function is the presence of Coulomb and Fermi hole.[13] Due to electrostatic Coulomb repulsion, motion of electrons is correlated and the probability of finding two electrons at the same point in space is zero. This correlation is known as Coulomb hole and an electron is said to be surrounded by a Coulomb hole with respect to all other electrons. As a consequence, a many-electron wave-function satisfying electronic Schrödinger equation explicitly shows presence of Coulomb hole by vanishing when spatial coordinates of any two electrons coincide. While any arbitrary many-electron wave-function does not show Coulomb hole, requirement of anti-symmetry gives raise to a correlation effect closely resembling it.

According to this, the probability of finding two electrons having parallel spins to be at the same point in space is zero. This feature is known as Fermi hole, and for electrons with parallel spin it replaces, to some extent, the corresponding Coulomb hole.

I.3.2 The Hartree-Fock approximation

The Hartree-Fock (HF) approximation[2,58] is central to all attempts at finding and describing approximate solutions to the electronic Schrödinger equation. It is based on the fact that stationary states of many systems, especially ground states of closed-shell atoms and molecules where all electrons are paired, can be well described by a single determinant.

$$\Phi_0(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N)=\tfrac{1}{\sqrt{N!}}\,\|\,\chi_1(\vec{x}_1),\chi_2(\vec{x}_2),\ldots,\chi_N(\vec{x}_N)\,\| \tag{1.7}$$

The HF method emerges when variational principle is used to find the best wave-function of the form of a determinant as in Eq (1.7) which makes electronic energy $\langle\Phi_0\,|\,\hat{H}_{el}\,|\,\Phi_0\rangle$ stationary with respect to variations in spin-orbitals. It is known that this procedure leads to certain integro-differential equations, referred to as the HF equations, defining the optimal spin-orbitals that make $\langle\Phi_0\,|\,\hat{H}_{el}\,|\,\Phi_0\rangle$ stationary while keeping them orthonormal. The HF equations can be written as eigenvalue equations of some effective one-electron operator $\hat{f}$ known as the Fock operator.[2]

$$\hat{f}(x)\chi_a(x)=\varepsilon_a\chi_a(x) \tag{1.8}$$

$$\hat{f}(x)=-\tfrac{1}{2}\nabla^2-\sum_{A=1}^{M}\frac{Z_A}{\|\vec{r}-\vec{R}_A\|}+v_{HF}(x) \tag{1.9}$$

$$v_{HF}(x)=\sum_{b=1}^{N}J_b(x)-\sum_{b=1}^{N}K_b(x) \tag{1.10}$$

$$J_b(x)\chi_a(x) = \int dx' \frac{\chi_b^*(x')\chi_b(x')}{|x - x'|}\chi_a(x) \tag{1.11}$$

$$K_b(x)\chi_a(x) = \int dx' \frac{\chi_b^*(x')\chi_a(x')}{|x - x'|}\chi_b(x) \tag{1.12}$$

Here, $v_{HF}(x)$ is known as HF potential. It is the average potential or the field experienced by an electron in presence of all other electrons. It includes a classical local potential $J_b(x)$ describing average Coulomb interaction of an electron at x with another electron in orbital χ_b. In addition, it includes a non-classical potential $K_b(x)$ resulting from anti-symmetry requirement and is known as exchange potential. It has no classical interpretation, and its effect is to generate highly non-local interactions resulting from exchange of coordinates of an electron in any orbital with coordinates of another electron in orbital χ_b. Since HF potential depends on spin-orbitals of other electrons or the Fock operator depends on its eigenfunctions, HF equations are non-linear and are solved in an iterative procedure known as self-consistent field (SCF) method. An initial guess of spin-orbitals is used to calculate approximate HF potential and Fock operator which are in turn used to obtain a new set of spin-orbitals. This procedure is repeated until some self-consistency is achieved between successive iterations.

Solution of HF equations Eq (1.8)-(1.12) yields an orthonormal set of HF spin-orbitals $\{\chi_i, i = 1,\ldots,\infty\}$ with corresponding orbital energies $\{\varepsilon_i\}$. The N spin-orbitals $\{\chi_a, a = 1,\ldots,N\}$ with lowest energies are referred to as occupied (or hole orbitals) and the remaining set of spin-orbitals $\{\chi_r, r = N+1,\ldots,\infty\}$ are referred to as unoccupied (or virtual or particle) orbitals. The Slater determinant formed with occupied spin-orbitals is the HF wave-function which approximates a stationary state of the Hamiltonian. Although some excited states well approximated by a single determinant may be obtained, in practice it is the ground state that is usually reached in an SCF procedure. Therefore, HF wave-function usually serves as an approximation for ground states of a non-degenerate many-electron systems.

HF equations can be exactly solved as non-linear integro-differential equations only for atoms.[2] For molecules, following Roothan,[59] a finite set of spatial basis functions $\left\{\phi_\mu(\vec{r}), \mu = 1, \ldots, K\right\}$ are introduced to expand the spatial part of spin-orbitals. This converts the HF equations into a set of matrix eigenvalue equations for the expansion coefficients, which are solved by an iterative SCF procedure. Different explicit forms for spin-orbitals lead to different variants of HF methods. Use of restricted set of spin-orbitals obtained by associating different spin-functions (spin-up or spin-down) to a set of spatial orbitals results in restricted HF (RHF) method, and leads to Roothan equations.[59] Further, if all the electrons are paired in the HF determinant this is referred to as closed-shell RHF method. If there are one or more unpaired electrons, it is referred to as open-shell RHF (or ROHF) method. On the other hand, use of unrestricted set of orbitals results in unrestricted HF (UHF) method and leads to Pople-Nesbet equations.[60] While a RHF or ROHF determinant is a pure eigenfunction of total spin operator $\hat{S}^2$, an UHF determinant, in general, is not.

The physical significance of HF orbital energies is provided by the Koopman's theorem on first ionization potentials and electron affinities of HF ground state.[2] According to this theorem, orbital energy ε_a of an occupied orbital χ_a in N-electron HF ground state is negative of the ionization potential required to produce $(N-1)$-electron determinant with same occupied orbitals except the orbital χ_a. Likewise, electron affinities can be related to energies of unoccupied orbitals. In practice, ionization potentials are better described than electron affinities due to fortuitous cancellation relaxation and correlation errors.[2] Another important result in HF theory is the Brillouin's theorem[2] which states that singly excited determinants obtained by promoting an electron from an occupied orbital to a virtual orbital does not directly interact (through the Hamiltonian) with the HF ground state. This result can be used as a defining condition for HF approximation.[3,33a]

The essence of HF approximation is that it involves replacement of the complicated many-electron problem by an effective one-electron problem in which electron repulsion is treated in an average way. This leads to a simple picture of molecular orbital (MO) theory with electrons occupying different orbitals. Apart from its own importance in quantum chemistry, the HF approximation usually constitutes a first step towards more accurate approximations.

I.3.3 Correlation energy and the configuration interaction method

The HF method recovers most portion of the exact ground state energy of atoms and molecules, and successfully explains many of their properties. The difference between exact energy of a state and its HF energy in the limit of basis set approaching completeness is referred to as correlation energy of the state.[13] It arises due to the fact that HF method is still an effective one-particle (or mean-field) method and can not fully account for instantaneous electron repulsion. Correlation energy is comparable to binding energy of outer shell valence electrons which are responsible for optical and chemical properties of atoms and molecules. In order to understand such properties even qualitatively, it is often necessary to go beyond HF method to treat atoms and molecules as true many-body systems.

Configuration interaction (CI)[13-15] is conceptually the simplest and traditional method to recover correlation energies. It is based on wave-function expansion in Eq

(1.6) and use of linear variation method to determine the expansion coefficients. It is often convenient to rewrite expansion Eq (1.6) in terms of a reference determinant Φ_0 and different excited determinants obtained by systematically replacing increasing number of occupied orbitals in Φ_0 by virtual orbitals.

$$\Psi = \Phi_0 + \sum_{a,r} C_a^r \Phi_a^r + \sum_{a>b,r>s} C_{ab}^{rs} \Phi_{ab}^{rs} + \cdots \tag{1.13}$$

Here, the intermediate normalization convention $\langle \Phi_0 | \Psi \rangle = 1$ has been used. The orbital labels $a, b, \ldots$ $(r, s, \ldots)$ refer to occupied (unoccupied) orbitals in reference determinant Φ_0. The determinant Φ_a^r is a singly excited determinant obtained by replacing occupied orbital χ_a in Φ_0 by unoccupied orbital χ_r. Similarly, Φ_{ab}^{rs} is a doubly excited determinant. The orbitals used in the above expansion are often chosen to be HF orbitals, and reference determinant Φ_0 is then the corresponding HF determinant. Although such a choice is not necessary, it is convenient and leads faster convergence in cases where HF determinant is really dominant one.

Use of linear variation method to determine expansion coefficients is known to result in eigenvalue problem (or equivalently diagonalisation) for the Hamiltonian matrix defined over all the determinants.[2] Matrix elements of Hamiltonian between any two Slater determinants are evaluated by using Slater-Condon rules.[2] When all possible excited determinants within a given basis set are included, it is referred to as the Full-CI method. While lowest eigenvalue and eigenvector of full-CI Hamiltonian matrix correspond to the ground state, rest of the eigenvalues and eigenvectors correspond to different excited states.

The full-CI method provides, in principle, a simple and exact solution of many-electron problem within a given basis set. However, it is not possible to include all the excited determinants in a practical computation. Even for small molecules with basis sets of moderate size, the number of excited determinants rapidly increases. Furthermore, it is known that larger basis sets are necessary to obtain accurate correlation energies.[1-2] Therefore, full-CI is computationally impractical and some kind of truncation of the set of excited determinants becomes necessary. Any such truncation means that resulting excited states are poorly represented. A commonly employed truncation scheme restricts excited determinants to only doubles or singles and doubles, and the resulting methods are referred to as CI doubles (CID) or CI singles and doubles (CISD). These are specially suited for ground states (or for states where the reference determinant is dominant), and recovers a significant portion of its correlation energy within the given basis set.[13]

Modern approaches to CI are far more advanced and considerably different from the traditional procedure involving complete diagonalisation of the Hamiltonian matrix. Firstly, the Slater determinants used in traditional CI are in general not pure spin eigenfunctions. Due to spin-free nature of electronic Hamiltonian, use of spin-adapted N-electron functions referred to as configuration state functions (CSF) is known to be efficient.[14-15] Two different approaches for construction of spin-adapted CSF have been developed. One approach, developed by Paldus and coworkers, is termed as the unitary group approach (UGA).[61] It is based on realization of CSF as a basis of the irreducible representation spaces of an underlying unitary group.[62] The UGA method is usually implemented using graphical representation of CSF and the rules for evaluation of Hamiltonian matrix elements presented by Shavitt.[63] An alternative to unitary group based approaches is the symmetric group approach (SGA) developed by Matsen,[62] and Karwowski.[64] Here, the CSF are constructed as basis for irreducible representations of

N-electron permutation group S_N. Graphical representation for SGA similar to the one in UGA has also been developed by Duck and Karwowski.[65]

Another feature of modern CI methods is the use of Davidson iterative diagonalisation technique to determine only few lowest (usually the ground state) eigenvalues and eigenvectors of the Hamiltonian matrix.[66] Here, unnecessary step of complete diagonalisation is averted by a procedure involving matrix-vector product of the Hamiltonian with a trial vector. A direct CI procedure advocated by Roos[67] is often used to compute this product thereby avoiding explicit construction and storage of Hamiltonian matrix elements. Further developments by Siegbahn[68] have involved combination of direct CI techniques with the graphical UGA to achieve efficiency in large scale CI calculations.

Another method related to CI is the multi-configuration self-consistent field (MCSCF) method.[2,69] An MCSCF wave-function is a truncated CI expansion where only a small number of selected determinants important for the description of a state are retained. Unlike CI, both the expansion coefficients and the orbitals are optimized to minimize the energy of MCSCF wave-function. This leads to equations somewhat similar in structure to the HF equations, and are solved by a SCF approach. A variant of MCSCF known as the complete active space MCSCF (CAS-SCF) method is frequently used.[70] Here, the selection of determinants to be included in the expansion is done by identifying a set of orbitals known as active or valence orbitals. All the determinants generated by distributing a given number of valence electrons among the all active orbitals are included in the MCSCF expansion. There are also several other variants of MCSCF method based on generalization of valence-bond approach of Heitler and London.[71]

I.3.4 Size-consistency and size-extensivity

Size-consistency and size-extensivity are two important criteria to be satisfied (or at least approximately satisfied) by any approximate quantum chemical method whenever energy calculations involving molecules of different sizes are to be compared, as in calculations of bond dissociation energies.[72] As defined by Pople and coworkers[73] and Bartlett,[22a] size-consistency of a method refers to its behaviour when it is applied to a collection of N non-interacting monomers. A method is termed size-consistent if the energy obtained in its application to this collection of monomers is N times the energy obtained in its separate application to the monomer. In other words, when a size-consistent method is applied to a molecule AB dissociating into two fragments A and B, the energy of the molecule calculated at the dissociating limit (or infinite separation limit) is equal to the sum of energies of both fragments calculated by separately applying the method to individual fragments.

$$E_{method}(AB) = E_{method}(A) + E_{method}(B) \tag{1.14}$$

In addition, size-consistency of a method is usually taken to mean that it also predicts a qualitatively correct dissociation curve. Clearly, size-consistency is a desirable feature for any approximate method. However, it is known that none of the truncated CI methods satisfy this requirement.[72] This is easily understood by applying CISD method to two infinitely separated He atoms. Since CISD method is equivalent to full-CI for two-electron systems, it yields exact energies for individual He atoms within the basis set employed. Due to CISD not being equivalent to full-CI for four electron systems, its application to the composite system of two infinitely separated He atoms, yields energy higher than the exact energy of the composite system. Therefore, CISD is not a size-consistent method. It can be shown that the closed-shell RHF method is size-consistent with respect to dissociation into closed-shell fragments, as in the example considered above.

Size-extensivity, a concept related to size-consistency, refers to mathematical scaling of the energy with the number of electrons.[30,72,74] A method is size-extensive if the energy a many-electron system calculated with the method, even in the presence of interactions, is approximately proportional to the number of electrons N and becomes exact as $N \to \infty$. In other words, the energy and the error in energy should increase in proportion to the size of the system. Size-extensivity is especially important for methods of electron correlation. If a method is not size-extensive, the error in correlation energy shows either sub-linear or super-linear dependence on the number of electrons (or equivalently the size of the system). In the former case, fraction of the exact correlation energy recovered per electron decreases as the size of the system increases eventually leading to zero correlation energy in the limit $N \to \infty$. In the latter case, the same fraction increases with the system size leading to prediction of infinite correlation energy per electron as $N \to \infty$. Therefore, all non-size-extensive methods show progressively unphysical behaviour as size of the system increases. Size-extensive methods are considered to be particularly appropriate for large systems, as they strive to recover a roughly constant fraction of exact correlation energy with increasing system size.

Studies on truncated CI methods have shown that the percentage of exact correlation energy within a given basis obtained in these methods decreases as the size of the molecule increases.[1] Therefore, truncated CI methods are not size-extensive. A simple method proposed by Davidson is often used to obtain an approximate a posteriori size-extensive correction to the calculated CI energies.

Another related concept that is useful in discussion on size-consistency and size-extensivity is separability. As discussed by Primas, separability is related to behaviour of certain quantities of a system composed of two sub-systems interacting with each other in the limit of vanishing interaction strength.[72,74-75] An additively separable quantity of the system, as the interaction vanishes, should be the sum of the same quantity for individual sub-systems. Similarly, a multiplicatively separable quantity should be the product of the same quantity for individual systems. For example, the total energy of many-electron systems is an additively separable quantity. Similarly, wave-function is multiplicatively separable. Clearly, separability condition is generalization of size-consistency condition on energy, with respect to an arbitrary division of the system into sub-systems.

While separability conditions are easily satisfied for quantities calculated from exact methods such as Full-CI, they do not hold in general for approximate ones. For example, it can be shown that wave-function calculated in any truncated CI method is not multiplicatively separable.[2] Consider the example of two infinitely separated He atoms as discussed above. In the anti-symmetrized product of CISD wave-functions of individual He atoms, quadruply excited determinants corresponding to simultaneous double excitation on each He atom appear. These determinants are not present in the CISD wave-function of the dimer. Therefore, as with CISD energy, CISD wave-function is also not separable. In fact, energy and wave-function separability are related to each other.

Historically, separability and size-extensivity were first discussed in studies on extended systems such as infinite nuclear matter and electron gas.[16,76] In such systems, the nature of correlation is different and its accurate treatment becomes necessary to obtain meaningful results. Furthermore, with number of particles tending to infinity, size-extensive treatment of correlation becomes essential. In this context, theories explicitly displaying their size-extensivity and allowing for accurate treatment of correlation effects were developed. Such explicitly size-extensive theories applicable in the $N \to \infty$ regime are referred to as many-body theories. They include many-body perturbation theory,[16-19] coupled-cluster theory,[19-25] Greens function and propagator based approaches,[77-78] equations-of-motion methods.[79]

The relevance and advantages of these many-body theories in quantum chemistry were realized by many early workers such as Kelly,[80] Cizek,[21a] and Freed.[81] This lead to formulation and application of rigorously size-extensive quantum chemical methods. It turns out that these theories also allow for accurate treatment of electron correlation effects in ground and low-lying excited states of atoms and molecules.

I.3.5 Second quantization, normal-ordering and diagrammatic techniques

Formal developments in many-body theories are greatly facilitated by using the algebraic and diagrammatic techniques of quantum field theory.[77] Important among them are the second quantization formalism, the concept of normal-ordering and Wick's theorem, the quasi-particle transformations and change of vacuum, and the diagrammatic representation introduced by Feynman.[77]

The second quantization formalism was first introduced by Dirac in his treatment on quantization of radiation fields. When applied to non-relativistic Schrödinger equation describing matter field, it results in a reformulation quantum theory of identical many-particles with an implicit incorporation of the symmetry or anti-symmetry principle associated with the particles. Expansion of resulting matter field quanta creation and annihilation operators in terms of a complete orthonormal set of one-particle basis functions (or spin-orbitals) leads to occupation number representation, where a many-particle wave-function is represented by specifying the number of particles occupied in each spin-orbital.

To describe second quantization formalism for the many-electron problem in quantum chemistry,[2,33a] a complete set of orthonormal spin-orbitals $\{\chi_i(x)\}$ are considered. For each spin-orbital χ_i, two operators $a_i^\dagger$ and a_i referred to as electron creation and annihilation operators respectively, are introduced. The electron creation operator $a_i^\dagger$, when operated on an N-electron determinant which does not contain χ_i, generates an $(N+1)$-electron determinant containing χ_i. Similarly, the electron annihilation operator a_i operating on an N-electron determinant containing χ_i, generates an $(N-1)$-electron determinant which does not contain χ_i. In other words, while $a_i^\dagger$ creates an electron in orbital χ_i, a_i destroys an electron occupying orbital χ_i. In addition, an vacuum state with no electrons in it, denoted by $|vac\rangle$, is postulated to exist with the following properties.

$$a_i^\dagger \,||\, \chi_j(\vec{x}_1), \chi_k(\vec{x}_2), \ldots, \chi_l(\vec{x}_N) \,||\, = \,||\, \chi_i(\vec{x}_1), \chi_j(\vec{x}_2), \chi_k(\vec{x}_3), \ldots, \chi_l(\vec{x}_{N+1}) \,|| \qquad (1.15)$$

$$a_i \,||\, \chi_i(\vec{x}_1), \chi_j(\vec{x}_2), \chi_k(\vec{x}_3) \ldots, \chi_k(\vec{x}_N) \,||\, = \,||\, \chi_j(\vec{x}_1), \chi_k(\vec{x}_2), \ldots, \chi_l(\vec{x}_{N-1}) \,|| \qquad (1.16)$$

$$\begin{aligned} a_i^\dagger |vac\rangle &= \,||\, \chi_i(\vec{x}) \,|| \\ a_i \,||\, \chi_i(\vec{x}) \,|| &= |vac\rangle \\ a_i |vac\rangle &= \langle vac| a_i^\dagger = 0 \\ \langle vac|vac\rangle &= 1 \end{aligned} \qquad (1.17)$$

Due to orthonormality of spin-orbitals, creation and annihilation operators associated with an orbital are adjoint of each other. Since determinants are anti-symmetric with respect to exchange of two orbitals, operation of a pair of creation operators (or a pair of annihilation operators) associated with two orbitals in a specific order results in a determinant which is negative of the determinant obtained by carrying out the operation in the reverse order. Similar considerations for a pair of operators consisting a creation and an annihilation operator lead to the following anti-commutation relations.

$$\begin{aligned} a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger &= \{a_i^\dagger, a_j^\dagger\} = 0 \\ a_i a_j + a_j a_i &= \{a_i, a_j\} = 0 \\ a_i^\dagger a_j + a_j a_i^\dagger &= \{a_i^\dagger, a_j\} = \delta_{i,j} \end{aligned} \tag{1.18}$$

Starting with the vacuum state and successively creating electrons in different orbitals by using associated creation operators, any determinant with a given number of electrons can be generated. The linear vector space spanned by determinants with different number of electrons, including the vacuum state, is known as Fock-space.[82-83] It is the direct sum of N-electron Hilbert spaces corresponding to different number of electrons. Creation and annihilation operators can be visualized to act within Fock-space. Any determinant Φ_I in Fock-space can be represented by sequence of creation operators acting on the vacuum, .i.e. $\Phi_I = a_i^\dagger a_j^\dagger a_k^\dagger \ldots |vac\rangle$.

It is known that the algebra of all linear operators on Fock-space is spanned by all possible distinct product operators $\left\{a_i^\dagger a_j^\dagger a_k^\dagger \ldots a_l a_m a_n \ldots\right\}$ obtained by taking product of a sequence of creation operators $a_i^\dagger a_j^\dagger a_k^\dagger \ldots$ with a sequence of annihilation operators $a_l a_m a_n \ldots$.[82] Second quantization representation of operators such as electronic Hamiltonian are obtained by expanding them in terms of these product operators. The matrix elements of a second quantized operator between any two determinants in Fock-space are demanded to be the same as the corresponding matrix elements the same operator evaluated using Slater rules. The second quantized form of electronic Hamiltonian in Eq (1.3) can be written as follows.

$$
\begin{aligned}
&\hat{H}_{el} = \sum_{i,j} \langle i \,|\, \hat{h} \,|\, j \rangle a_i^\dagger a + \frac{1}{2} \sum_{i,j,k,l} \langle ij \,|\, \hat{g} \,|\, kl \rangle a_i^\dagger a_j^\dagger a_l a_k \\
&\langle i \,|\, \hat{h} \,|\, j \rangle = \int d\vec{x}\, \chi_i^*(\vec{x}) \hat{h}(\vec{x}) \chi_j(\vec{x}) \\
&\langle ij \,|\, \hat{g} \,|\, kl \rangle = \int d\vec{x}_1 d\vec{x}_2 \chi_i^*(\vec{x}_1) \chi_j^*(\vec{x}_2) \hat{g}(\| \vec{x}_1 - \vec{x}_2 \|) \chi_k(\vec{x}_1) \chi_l(\vec{x}_2)
\end{aligned}
\qquad (1.19)
$$

An advantage of the above form of electronic Hamiltonian is that it is not dependent on the number of electrons and it applies to the whole of Fock-space. Matrix elements of second quantized operators (or a product of such operators) between any two Fock-space determinants are evaluated by using the concept of normal ordering[17,83] and commutation rules as in Eq (1.18). A sequence of creation and annihilation operators is said to be in normal-order if all the annihilation operators precede the creation operators. An example of normal-ordered operator is $a_i^\dagger a_j^\dagger a_l a_k$ present in Eq (1.19). The given Fock-space determinants are expanded in terms of creation operators to write the required matrix element as a vacuum expectation value of a general sequence of creation-annihilation operators. Such an operator sequence can be brought to normal-ordered form by using Eq (1.18) to anti-commute all annihilation operators onto the right side. Each time an annihilation operator associated with a spin-orbital is brought to the right of a creation operator associated with the same-spin orbital, two terms are generated. In the first term, referred to as contraction term, the two creation-annihilation operators are not present and are said to be contracted. The second term contains the two creation-annihilation operators anti-commuted. This process of moving annihilation operators to the right is continued for the left over operator sequences in both these terms until they are fully contracted or reach normal-ordered form. Since vacuum expectation value of a normal-ordered operator vanishes, the matrix element is non-zero only when all annihilation and creation operators are fully contracted with each other.

The above process is simplified by applying Wick's theorem.[17,77,83] This theorem states that any general operator sequence A is equal to the sum of its normal-ordered form $\{A\}$ and normal-ordered form $\overbracket{\{A\}}$ of its all possible contracted terms.

$$A = \{A\} + \overbracket{\{A\}} \tag{1.20}$$

The generalized form of Wick's theorem is often useful. It states that the product of two normal- ordered operators X and Y is given as follows.

$$XY = \{XY\} + \{\overbracket{XY}\} \tag{1.21}$$

The term $\{\overbracket{XY}\}$ represents normal-ordered form of product of X and Y with all possible contraction between them excluding self-contractions. The normal-ordering and Wick's theorem lead to graphical representation of the process of matrix element evaluation. A normal-ordered operator such as Hamiltonian in Eq (1.19) can be graphically depicted by using a vertex to represent its matrix element such as $\langle ij \,|\, \hat{g} \,|\, kl \rangle$. The normal-ordered operator sequence associated with the matrix element can be represented by attaching certain labeled directed lines to the vertex. Each annihilation operator is represented by an upward directed line coming into the vertex. Similarly, an upward directed line going out of the vertex represents corresponding creation operator. The generalized Wick's theorem in Eq (1.21) can be graphically represented by placing the graphical form of X on top of Y. A contraction between X and Y is represented by a line joining an outgoing line on X with an incoming line on Y with a matching orbital label. Consequently, the second term of Eq (1.21) can be represented by drawing all possible connected graphs with lines connecting vertices of X and Y (referred to as internal lines). Similarly, the first term can be represented by all disjoint graphs with no connections between the two vertices. The required matrix element is obtained by selecting graphs with a set of external incoming lines matching the occupied orbitals on right side determinant and a set of external outgoing lines matching the occupied orbitals on left side determinant. Further simplifications are introduced by disregarding Pauli's exclusion principle for intermediate states between the two operators and assuming unrestricted summation convention over labels of internal lines of graphs.

In quantum chemistry, most often interest is not in absolute occupancy of determinants but rather in occupancy of determinants relative to a reference determinant Φ_0 as in CI expansion Eq (1.13). Relative occupancies are considered by carrying out a transformation of creation-annihilation operators to define quasi-particles, i.e., holes and particles.[17,82-83] This is equivalent to change of vacuum from $|vac\rangle$ to Φ_0. Occupied orbitals in Φ_0 are referred to as hole orbitals and unoccupied orbitals are referred to as particle orbitals. Creating a hole is defined as annihilating an electron present in the corresponding hole orbital. Similarly, annihilating a hole is defined as creating an electron in a hole orbital. Particle creation and annihilation processes are respectively identical to electron creation and annihilation in particle orbitals. This defines a new set of hole-particle creation-annihilation operators $\left\{b_i^\dagger, b_i\right\}$, with $b_i^\dagger = a_i^\dagger$ and $b_i = a_i$ for particles and $b_i^\dagger = a_i$ and $b_i = a_i^\dagger$ for holes, obeying the same set of anti-commutation rules as $\left\{a_i^\dagger, a_i\right\}$. With this, the new vacuum Φ_0 is a state with no holes or particles present in it and all other determinants are states have some holes and particles.

The concept of normal-ordering, Wick's theorem and the associated graphical representations are easily extended to hole-particle operators.[17] When normal-ordered with respect to Φ_0, the electronic Hamiltonian in Eq (1.19) is written as follows.

$$\begin{aligned}
&\hat{H}_{el} = H_0 + \hat{H}_N \\
&H_0 = \langle \Phi_0 | \hat{H}_{el} | \Phi_0 \rangle \\
&\hat{H}_N = \sum_{i,j} \langle i | \hat{u} | j \rangle \{a_i^\dagger a_j\} + \frac{1}{2} \sum_{i,j,k,l} \langle ij | \hat{g} | kl \rangle \{a_i^\dagger a_j^\dagger a_l a_k\} \\
&\langle i | \hat{u} | j \rangle = \langle i | \hat{h} | j \rangle + \sum_{a \in \Phi} \langle ia | \hat{g} | ja \rangle - \langle ia | \hat{g} | aj \rangle
\end{aligned} \tag{1.22}$$

Here, curly brackets represent normal-ordering of enclosed sequence of operators with respect to Φ_0. H_0 is the vacuum expectation value and $\hat{H}_N$ is the normal-ordered form of electronic Hamiltonian. For graphical representation of such operators, holes are represented by downward directed lines and particles by upward directed lines. Hole creation and annihilation operators are respectively represented by hole lines terminating on or emanating from the operator vertex. Representation for particles are same as earlier. With this, the generalized Wick's theorem can be used obtain graphical representation of operator products and their matrix elements between any two arbitrary determinants.

In second quantization formalism, the CI expansion Eq (1.13) can be rewritten by defining a normal-ordered operator C, split up into its various I-body components, C_I.

$$\begin{aligned}
&| \Psi \rangle = (1 + C) | \Phi_0 \rangle \\
&C = C_1 + C_2 + \cdots + C_N \\
&C_I = \frac{1}{(I!)^2} \sum_{\substack{a,b,\ldots \\ r,s,\ldots}} c_{ab\ldots}^{rs\ldots} \{a_r^\dagger a_s^\dagger \ldots a_b a_a\}
\end{aligned} \tag{1.23}$$

The operator $1+C$ is known as wave-operator, and C is known as correlation operator. Clearly, their determination is equivalent to determination of the linear expansion coefficients in Eq (1.13). Substitution of above ansatz into N-electron Schrödinger equation followed by left projection onto various N-electron determinants hole-particle excited with respect to Φ_0 leads to the following equations for C, and the correlation energy $\Delta\mathcal{E}_{corr}$.

$$\Delta\mathcal{E}_{corr} = \mathcal{E} - H_0 = \langle\Phi_0 \,|\, \hat{H}_N \left(1 + C\right) | \,\Phi_0\rangle \tag{1.24}$$

$$\langle\Phi_{ab\ldots}^{rs\ldots} \,|\, \hat{H}_N \left(1 + C\right) | \,\Phi_0\rangle = \Delta\mathcal{E}_{corr} \langle\Phi_{ab\ldots}^{rs\ldots} \,|\, C \,|\, \Phi_0\rangle \tag{1.25}$$

All the matrix elements in these equations can be evaluated using the generalized Wick's theorem. Size-inextensive nature of truncated CI methods can be seen in the associated graphical representation. For $\Delta\mathcal{E}_{corr}$ to be size-extensive, its final graphical form must consist of fully connected closed diagrams.[74,83] Such diagrams are known to scale properly with the size of the system. Their presence in energy expression directly reflects the size-extensivity of the method. Although energy diagrams in Eq (1.24) appear to be this form, subsequent iterative substitution of expressions for $\langle\Phi_{ab\ldots}^{rs\ldots} \,|\, \hat{C} \,|\, \Phi_0\rangle$ in Eq (1.25) results in certain disconnected diagrams. This happens due to the presence of $\Delta\mathcal{E}_{corr}$ on right hand side of Eq (1.25). Such disconnected diagrams have parts which are closed and connected, and are referred to as unlinked diagrams. These unlinked diagrams are known to be responsible for the size-inextensive behaviour of truncated CI methods.

To summarize, for the many-electron problem relevant to quantum chemistry, second quantization formalism merely represents a change of picture from electronic configurations or Slater determinants interacting via the many-electron Hamiltonian to that of a matter field of electrons interacting via the inter-electron coulomb repulsion potential, and described by an anti-commuting set of creation and annihilation operators. The main advantages of second quantization formulation are 1. The anti-symmetry principle is easily incorporated into the picture. 2. The second quantized operators are independent of number of electrons, and therefore are suited to describe processes such as ionization where number of electrons changes. 3. Wicks theorem and associated graphical representation simplify implementation of the methods and help monitor their size-extensivity.

I.3.6 Many-body perturbation theory

Perturbation theory is another useful method to systematically incorporate electron correlation effects.[1-2,16-19,24] In this approach, the exact Hamiltonian $\hat{H}$ is partitioned into a zeroth-order Hamiltonian $\hat{H}_0$ and a small term $\hat{H}'$ known as perturbation. The stationary states $\{\Phi_I\}$ and energies $\{E_I\}$ of the zeroth-order Hamiltonian as well as the perturbation matrix elements $\langle\Phi_I | H' | \Phi_J\rangle$ are all assumed to be known. The stationary states $\{\Psi_I\}$ and energies $\{\mathcal{E}_I\}$ of exact Hamiltonian $\hat{H}$ are sought to be determined in terms of these known quantities. For this, the existence of an one-to-one correspondence between stationary states and energies of $\hat{H}_0$ and $\hat{H}$ is assumed. This means that there is a parameter λ which when smoothly varied between 0 and 1 connects the eigenvalues and eigenvectors of $\hat{H}_0$ (for $\lambda = 0$) and $\hat{H}$ (for $\lambda = 1$). In perturbation theory, $\{\Psi_I\}$ and $\{\mathcal{E}_I\}$ are obtained by carrying out a Taylor series expansion of these quantities around $\lambda = 0$ which corresponds to the zeroth-order Hamiltonian. It is further assumed that $\hat{H}_0$ has been chosen to make the perturbation (or its matrix elements) small enough for the Taylor series to be convergent. In such cases, calculation of first few terms in the expansion yields sufficiently accurate approximation to the exact values.

In practice, it is possible to satisfy these requirements only for the ground state. For this reason, perturbation theory is mainly used to calculate correlation energy of the ground state of closed-shell systems. Usually, $\hat{H}_0$ is chosen to be an one-electron operator so that $\{\Phi_I\}$ are represented by determinants. When perturbative corrections to

HF ground state and energies are to be calculated, $\hat{H}_0$ is chosen as the sum of Fock operators, i.e., $\hat{H}_0 = \sum_i \hat{f}(i)$. This is known as Moller-Plesset (MP) partitioning scheme. In this case, Φ_0 is the dominant HF determinant for the ground state, E_0 is the zeroth-order energy which is the sum of energies of occupied HF orbitals, and $\{\Phi_I, I \neq 0\}$ are the different excited determinants as in CI expansion Eq (1.13).

Assuming intermediate normalization between zeroth-order ground state Φ_0 and the corresponding exact ground state Ψ_0, .i.e., $\langle \Phi_0 | \Psi_0 \rangle = 1$, the difference $\Delta\mathcal{E}_0$ between the exact ground state energy $\mathcal{E}_0$ and zeroth-order energy E_0 can be written as follows.

$$\mathcal{E}_o - E_0 = \Delta\mathcal{E}_0 = \langle \Phi_0 | \hat{H}' | \Psi_0 \rangle \tag{1.26}$$

In perturbation theory, ΔE_0 and Ψ_0 are written as a series of corrections terms of increasingly higher order in perturbation.

$$\Delta\mathcal{E}_0 = \Delta\mathcal{E}_0^{(1)} + \Delta\mathcal{E}_0^{(2)} + \cdots + \Delta\mathcal{E}_0^{(n)} + \cdots \tag{1.27}$$

$$\Psi = \Phi_0 + \Psi_0^{(1)} + \Psi_0^{(2)} + \cdots + \Psi_0^{(n)} + \cdots \tag{1.28}$$

$$\Delta\mathcal{E}_0^{(n)} = \langle \Phi_0 | \hat{H}' | \Psi_0^{(n-1)} \rangle \tag{1.29}$$

Here, $\Delta\mathcal{E}_0^{(n)}$ and $\Psi_0^{(n)}$ are the n-th order energy and wave-function corrections for the ground state respectively and contain n-th power of the perturbation $\hat{H}'$. Different perturbation theories differ in explicit expressions for $\Delta\mathcal{E}_0^{(n)}$ and $\Psi_0^{(n)}$. Denoting the projectors for Φ_0 and $\{\Phi_I, I \neq 0\}$ by P_0 and Q_0 respectively, a manipulation of Schrödinger equation leads to the Brillouin-Wigner perturbation theory (BWPT)[17] with following expression for $\Delta\mathcal{E}_0^{(n)}$ and $\Psi_0^{(n)}$.

$$\Delta\mathcal{E}_0^{(n)} = \langle \Phi_0 | \hat{H}' \left(\frac{Q_0}{\mathcal{E}_0 - \hat{H}_0} \hat{H}' \right)^{n-1} | \Phi_0 \rangle \tag{1.30}$$

$$\Psi_0^{(n)} = \left(\frac{Q_0}{\mathcal{E}_0 - \hat{H}_0} \hat{H}' \right)^n |\Phi_0\rangle \tag{1.31}$$

In BWPT, perturbation correction at any order depends on the exact ground state energy $\mathcal{E}_0$ which is a priori not known. Therefore, the expression for total energy up to a required order is used to setup an iterative self-consistent procedure for the determination of correlation energies and wave-functions.[17] By writing $\mathcal{E}_0$ in Eq (1.30) as $E_0 + \Delta\mathcal{E}_0$, and expanding and rearranging the terms involving denominators, another series of type Eq (1.27)-(1.28) with the following expressions for $\Delta\mathcal{E}_0^{(n)}$ and $\Psi_0^{(n)}$ is obtained.

$$\Delta\mathcal{E}_0^{(n)} = \langle\Phi_0 | \hat{H}' \left(\frac{Q_0}{E_0 - \hat{H}_0} \left(\hat{H}' - \Delta\mathcal{E}_0 \right) \right)^{n-1} |\Phi_0\rangle \tag{1.32}$$

$$\Psi_0^{(n)} = \left(\frac{Q_0}{E_0 - \hat{H}_0} \left(\hat{H}' - \Delta\mathcal{E}_0 \right) \right)^n |\Phi_0\rangle \tag{1.33}$$

The Rayleigh-Schrödinger perturbation theory (RSPT)[16-17] series is obtained from the above series by expanding $\Delta\mathcal{E}_0$ in Eq (1.32)-(1.33) in powers of the perturbation $\hat{H}'$ and collecting all the terms containing a fixed power of $\hat{H}'$. Compact expressions for energy and wave-function corrections at each order can be derived. In contrast to BWPT, these expressions contain only the known unperturbed ground state energy E_0 in the denominators of resolvents. Therefore, they can be directly applied without resorting to iterative procedures.

Applications of RSPT based on RHF vacuum employ Møller-Plesset partitioning scheme where the zeroth-order Hamiltonian is a diagonal operator expressed in terms of HF orbital energies. This considerably simplifies the expressions for energy and wave-function corrections and is referred to as the Møller-Plesset perturbation theory (MPPT).

The first-order energy correction is same in both BWPT and RSPT. When it is added to the zeroth-order energy E_0, the Hartree-Fock ground state energy is recovered. Correlation energies are obtained by applying these methods beyond first-order. Second-order MPPT (also known as MP2 method) for energy recovers considerable fraction of correlation energy for closed-shell atoms and molecules. The first-order MPPT correction to wave-function consists of only doubly excited determinants, with singly excited determinants being absent due to Brillouin's theorem.[2,17] It can be shown that, singly and triply excited determinants start to contribute to energy corrections from third-order onwards.[17]

However, it difficult to employ RSPT or BWPT methods beyond third-order. Furthermore, such a direct application entails size-extensivity problems. As in the case of truncated CI methods, the presence of exact ground state energy $\mathcal{E}_0$ in BWPT makes it a size-inextensive method thereby limiting its applications. In case of RSPT, certain size-inextensive terms (known as unlinked terms) do appear in the conventional energy and wave-function correction expressions beyond second order. For the third and fourth order RSPT, Bruecker[76] algebraically showed that these unlinked terms within each order cancel amongst each other. In the graphical representation of RSPT series, such unlinked terms appear as disconnected graphs with closed sub-graphs and are known as unlinked diagrams. Goldstone[83a] and Hugenholtz[83b] diagrammatically proved that, at each order of RSPT, such unlinked diagrams cancel amongst each other. This result is known as the linked diagram theorem.

Therefore, the RSPT is size-extensive provided unlinked terms are systematically removed in each order. This requires graphical representation of RSPT and the use of linked diagram theorem. The resulting form of RSPT explicitly exhibits its size-extensive nature through the presence of only linked diagrams and is referred to as many-body perturbation theory (MBPT). The MBPT series for the ground state energy consists of a set of fully connected closed diagrams with each diagram originating from the energy correction expression of a certain order of perturbation. Likewise, the ground state wave-function is represented by a fully linked set of upward open diagrams, .i.e., those which do not contain closed connected sub-diagrams. Such linked diagrams are either fully connected open diagrams or they are disconnected with fully connected open sub-diagrams.

First applications of MBPT to atoms were carried out by Kelly.[80] Conventional MBPT calculations involve calculating all energy diagrams up to a given order. It is well-known that the MBPT series is slowly converging, and it becomes necessary to include higher-order terms. Inclusion of such terms through conventional techniques is not feasible due to rapid proliferation of the number of terms to be included at each order. However, the diagrammatic nature of MBPT enables to introduce the concept of partial summation technique to alleviate this problem. Instead of summing up all diagrams at a given order, diagrams contributing to different perturbation orders are summed. It has been shown that certain classes of diagrams can be summed to up to infinite order.[19] Such a partial infinite summation technique is an efficient way to selectively include certain necessary higher-order contributions. In most cases, it yields correlation energies which are more accurate as compared to conventional order-by-order type of approaches, and leads to coupled-cluster theory.

I.3.7 The coupled-cluster theory

The coupled-cluster theory was first introduced in nuclear physics. Using diagrammatic MBPT, Hubbard[84c] showed that the exact ground state wave-function of many-electron system can be written in an exponential form as follows.

$$|\Psi_0\rangle = e^{T}\,|\Phi_0\rangle \tag{1.34}$$

The operator T is known as cluster operator. Diagrammatically, it contains only the upward open connected MBPT wave-function diagrams. The disconnected diagrams with connected open sub-diagrams appearing in MBPT wave-function are properly generated by the exponential.[17,19,23-25] The cluster operator can be decomposed into various connected I-body components T_I as follows.

$$\begin{aligned} T &= T_1 + T_2 + \cdots + T_N \\ T_I &= \frac{1}{(I!)^2} \sum_{\substack{a,b,\ldots \\ r,s,\ldots}} t_{ab\ldots}^{rs\ldots} \{a_r^\dagger a_s^\dagger \ldots a_b a_a\} \end{aligned} \tag{1.35}$$

The I-body cluster operator T_I, acting on vacuum $|\Phi_0\rangle$, produces a linear combination of I-tuply hole-particle excited determinants. The cluster amplitudes $t_{ab\ldots}^{rs\ldots}$ are assumed to be anti-symmetric with respect to exchange of orbital labels among the occupied and virtual orbitals. The above ansatz in Eq (1.34)-(1.35) can be viewed as an exponential parameterization of the CI ansatz Eq (1.23) with the following relations between T_I and C_I.

$$\begin{aligned} C_1 &= T_1 \\ C_2 &= T_2 + \tfrac{1}{2!}T_1^2 \\ C_3 &= T_3 + T_1T_2 + \tfrac{1}{3!}T_1^3 \\ C_4 &= T_4 + T_1T_3 + \tfrac{1}{2}T_1^2T_2 + \tfrac{1}{2}T_2^2 + \tfrac{1}{4!}T_1^4 \\ &\vdots \end{aligned} \tag{1.36}$$

The above relations hold only for the exact wave-functions.[23,25,33a,] Clearly, with exponential parameterization, any excitation term in CI wave-function has been decomposed into a purely connected excitation term along with disconnected products of all lower-body excitations. Diagrammatic contributions to purely connected I-body component T_I come from fully connected open I-th order MBPT diagrams.

A scheme to directly compute the cluster amplitudes was first formulated in nuclear physics by Coester and Kummel.[85] It is known as coupled-cluster (CC) theory. Later on, Cizek and Paldus[21] brought these ideas into quantum chemistry along with relevant approximations and diagrammatic approach for the derivation of CC equations. At the same time, the usefulness of cluster structure of many-electron wave-functions for electron correlation in atoms and molecules was noticed and studied from a different perspective by Sinanoglu,[20] Nesbet,[86] and Meyer[87] who proposed slightly different methods related to CC method.

In CC method, cluster amplitudes are treated as independent parameters to be determined without assigning them any a priori perturbative content. Substitution of Eq (1.34) into Schrödinger equation with normal-ordered Hamiltonian leads to,

$$\hat{H}_N e^T |\Phi_0\rangle = \Delta\mathcal{E}_{corr} e^T |\Phi_0\rangle \tag{1.37}$$

Left projection of this equation with vacuum $|\Phi_0\rangle$ and various hole-particle excited determinants $|\Phi_{ab...}^{rs...}\rangle$ leads to the following equations to determine the correlation energy and the cluster amplitudes.

$$\Delta\mathcal{E}_{corr} = \langle\Phi_0 | \hat{H}_N e^T | \Phi_0\rangle \tag{1.38}$$

$$\langle\Phi_{ab...}^{rs...} | \hat{H}_N e^T | \Phi_0\rangle = \Delta\mathcal{E}_{corr} \langle\Phi_{ab...}^{rs...} | e^T | \Phi_0\rangle \tag{1.39}$$

Making use of the Wick's theorem along with the fact that e^T is normal-ordered, the above equations can be diagrammatically represented. This shows that the correlation energy in Eq (1.38) is diagrammatically represented by a set of closed connected diagrams in which each cluster operator being connected to the Hamiltonian vertex. As in the case of CI Eq (1.25), the term containing $\Delta\mathcal{E}_{corr}$ on the right hand side of Eq (1.39) is unlinked. Diagrammatic analysis of the term on the left hand side of Eq (1.39) shows that, due to the presence of exponential, it contains unlinked terms which exactly cancel the unlinked terms on the right hand side. Therefore, the left hand side of Eq (1.39) contains entirely linked open diagrams and Eq (1.38)-(1.39) can be written as follows.

$$\Delta\mathcal{E}_{corr} = \langle\Phi_0 | \hat{H}_N e^T | \Phi_0\rangle_{closed,connected} \tag{1.40}$$

$$\langle\Phi_{ab\ldots}^{rs\ldots} | \hat{H}_N e^T | \Phi_0\rangle_{open,linked} = 0 \tag{1.41}$$

Further analysis shows that the disconnected terms in Eq (1.41) for a specific hole-particle excitation disappear due to hierarchy of Eq (1.41) corresponding to lower hole-particle excitations. For single excitations, Eq (1.41) does not contain any disconnected terms and can be written as $\langle\Phi_a^r | \hat{H}_N e^T | \Phi_0\rangle_{open,connected} = 0$. The disconnected terms in Eq (1.41) for double excitations occur as product of a connected single excitation term $\langle\Phi_a^r | \hat{H}_N e^T | \Phi_0\rangle_{open,connected}$ with a singly excited cluster amplitude t_b^s and hence disappear from the final equations. Similar considerations apply for disconnected terms involving higher excitations and only connected open diagrams survive in Eq (1.41). This leads to the following completely connected CC equations.

$$\Delta\mathcal{E}_{corr} = \langle\Phi_0 | \hat{H}_N e^T | \Phi_0\rangle_{closed,connected} \tag{1.42}$$

$$\langle\Phi_{ab\ldots}^{rs\ldots} | \hat{H}_N e^T | \Phi_0\rangle_{open,connected} = 0 \tag{1.43}$$

Since the cluster operators commute, they can not be connected with each other. This means that in the diagrammatic representation of Eq (1.43), each cluster operator present has to be connected to the Hamiltonian vertex. Being an at most two-body operator, the Hamiltonian can have a maximum of four lines for such connections. Consequently, each term of Eq (1.43) can have a maximum of four cluster operators. Therefore, CC equations are algebraic nonlinear equations in unknown cluster amplitudes, and are of at most quartic power. It can be further shown that expression for correlation energy Eq (1.42) contains only one-body and two-body cluster operators. These cluster operators are in turn coupled to higher-body cluster operators via the CC Eq (1.43).

An alternative derivation of CC equations offering a different perspective of the CC theory is often used in literature.[19,21,25] It involves pre-multiplication of Eq (1.37) by e^{-T} to obtain the following equations.

$$e^{-T}\hat{H}_N e^{T} \,|\, \Phi_0\rangle = \Delta\mathcal{E}_{corr} \,|\, \Phi_0\rangle \tag{1.44}$$

The non-hermitian operator $\hat{\bar{H}} = e^{-T}\hat{H}_N e^{T}$ is just the original Hamiltonian $\hat{H}_N$ similarity transformed ($X^{-1}AX$) by an invertible operator $X = e^{T}$. Therefore, Eq (1.44) can be viewed as an eigenvalue equation for the similarity transformed Hamiltonian $\hat{\bar{H}}$. It is well known that similarity transformation of an operator does not change its eigenvalues. The CC equations can be obtained by left projection of Eq (1.44) by the vacuum $|\, \Phi_0\rangle$ and various hole-particle excited determinants $|\, \Phi_{ab\ldots}^{rs\ldots}\rangle$.

$$\Delta\mathcal{E}_{corr} = \langle \Phi_0 \,|\, e^{-T}\hat{H}_N e^{T} \,|\, \Phi_0\rangle \tag{1.45}$$

$$\langle \Phi_{ab\ldots}^{rs\ldots} \,|\, e^{-T}\hat{H}_N e^{T} \,|\, \Phi_0\rangle = 0 \tag{1.46}$$

It can be shown that the above equations are identical to CC equations Eq (1.42)-(1.43). By making use of the Baker-Campbell-Hausdorf (BCH) formula for $e^{-B}Ae^{B}$, the similarity transformed Hamiltonian operator $\hat{\bar{H}} = e^{-T}\hat{H}_N e^{T}$ can be written as follows.[19,25]

$$\hat{\bar{H}} = e^{-T}\hat{H}_N e^{T} = \hat{H}_N + [\hat{H}_N, T] + \tfrac{1}{2!}[[\hat{H}_N, T], T] + \cdots \tag{1.48}$$

Due to the two-body nature of $\hat{H}_N$ and commutativity of cluster operators, this series can be shown to terminate after four-fold commutation. The connected nature of correlation energy and cluster amplitudes is explicitly revealed by the presence of commutators in Eq (1.48). With the Hamiltonian $\hat{H}_N$ being connected, its commutation with cluster operators generates only connected terms, eventually leading to a completely connected series.

The Eq (1.46) defining cluster amplitudes can be viewed as condition to make the lower triangular block (or a major part thereof) of the $\hat{\bar{H}}_N$ to vanish. This facilitates finding the corresponding eigenvalue of $\hat{\bar{H}}_N$, which in turn is equivalent to calculating the correlation energy. Apart from directly showing the connected nature of correlation energy and cluster amplitudes through the use of BCH formula, this alternate derivation shows that CC method may be viewed as diagonalisation of a similarity transformed Hamiltonian to obtain correlation energy. Such a conceptual view point is also useful to understand various generalizations CC method for multi-reference cases as well as various equation-of-motion CC methods for excited states.[30,83]

As in the case of CI, the full cluster operator involving up to N-fold excitations can not be retained in practical applications and it has to be truncated. Since double excitations are dominant in the first-order MBPT wave-function based on closed-shell RHF vacuum $|\Phi_0\rangle$, the two-body cluster operator T_2 may be expected to be important.

For this reason, truncation of cluster operator to its two-body part .i.e., $T \cong T_2$ was the earliest approximation employed by Cizek who refers the resulting CC method as the coupled-pair many-electron theory (CPMET).[21a] In modern terminology, the CPMET is known as coupled-cluster doubles (CCD) method. The CC wave-function within $T \cong T_2$ approximation has also been studied by Sinanoglu who also refers the resulting method as CPMET.[20b] While Cizek adopts a non-variational strategy involving solution of Eq (1.43) for the determination of two-body cluster amplitudes, Sinanoglu uses a kind of stationary principle on dominant part of the energy functional. The CCD was also re-derived by Hurley from a different perspective.[4]

The CCD wave-function not only includes double excitations, but also higher-body excitations such as quadruple and hextuple excitations. However, the amplitudes of these higher-body excitations are not independent. They are represented as appropriate sum of products of amplitudes of all possible independent double excitations constituting the given higher-body excitation. The importance of quadruple excitations arising as two independent and simultaneous double excitations has been well emphasized by Sinanoglu in his CPMET developments.[20b] Due to its exponential nature, the CC wave-function naturally includes such excitations, and hence it may be considered to be a better representation as compared to its CI counterpart.

The major advantage of CC formulation is that unlike truncated CI methods, approximate CC methods obtained by using a truncated cluster operator are size-extensive and size-consistent. Since CC equations are represented by only connected open diagrams, it can be shown that the cluster operator calculated from these equations is additively separable. As a result, being represented by connected diagrams of the Hamiltonian with this cluster operator, the CC correlation energy is also additively separable, and hence is size-extensive. As discussed by Primas,[75] the CC wave-operator e^T, being exponential of additive separable cluster operator, is multiplicative separable. These properties ensure the size-consistency of CC method provided the vacuum $|\Phi_0\rangle$ properly separates under dissociation.[72]

First application of CPMET at semi-empirical level was presented by Cizek.[21a] First ab initio application of CC theory to study correlation effects in BH_3 was carried out by Paldus et al, who extended CPMET to approximately include connected one-body (singles) and three-body (triples) cluster operators.[89] Systematic development and applications of CCD method in spin-orbital form were initiated by Bartlett and coworkers,[88b] and Pople and coworkers.[88a] CC method with cluster operator truncated to include one-body and two-body cluster operators, .i.e., $T \cong T_1 + T_2$, referred to as CCSD method, was first implemented in spin-orbital form by Purvis and Bartlett. This not only enabled to assess the importance of disconnected triple excitations, but also allowed to explore the use of general non-canonical HF orbitals. Later on, Noga and Bartlett[91] carried out complete inclusion of up to connected triples cluster operator, .i.e., $T \cong T_1 + T_2 + T_3$, referred to as CCSDT method.[23] The CCD, CCSD and CCSDT methods represent a hierarchy of increasingly accurate CC methods. Kucharski and Bartlett extended this hierarchy further by including the connected quadruple cluster operator T_4 to obtain the CCSDTQ method.[92]

As mentioned earlier, CC equations are algebraic non-linear equations in cluster amplitudes. They are usually solved using Jacobi iterative schemes, with each iteration involving evaluation of products of cluster amplitudes with the Hamiltonian. Efficient factorization of CC equations along with matrix multiplication based techniques for evaluation of such products have been developed by various workers. The computational complexity of CCD and CCSD methods is $\sim N_o^{\,2} N_v^{\,4}$ floating point operations per iteration (N_o and N_v are the number of occupied and unoccupied orbitals respectively).[22c] This rapidly increases as higher-body connected cluster operators are added, as exemplified in CCSDT method scaling as $\sim N_o^{\,3} N_v^{\,5}$ and CCSDTQ method scaling as $\sim N_o^{\,4} N_v^{\,6}$.[22c]

The relation between CC and MBPT has been well studied.[24,25] It is known that each iteration CC equations generates an additional set of higher-order MBPT diagrams, both for energy and wave-function. Therefore, CC method can be viewed as a way to systematically sum selected classes of MBPT diagrams to infinite order. In other words, CC method is an indirect way to carry out a partial infinite-order summation of MBPT diagrams.[22c] This relation has been useful in devising computationally attractive approximations to CCSD and CCSDT methods. It can be shown that MBPT diagrams summed by CCSD method include all third-order MBPT diagrams. Therefore, CCSD method is correct through third-order MBPT. Likewise, it can be shown that CCSDT method is correct through fourth-order MBPT.[22c] A perturbative analysis of contribution of different terms in CCSDT equations to identify terms appearing at low-orders helps device computationally efficient iterative and non-iterative approximations to the full CCSDT method. The iterative CCSDT-1 and non-iterative CCSD(T) methods are such approximations, which have been popular and successful.[22c] Like CCSDT, both these methods are correct through fourth-order MBPT. However, they scale only as $\sim N_o^{\,3} N_v^{\,4}$ and hence are computationally less demanding by one order as compared to the full CCSDT method. The relation between CC and MBPT has been exploited to develop expressions for higher-order MBPT energy corrections.[24]

The CC method is closely related to pair correlation theories which originated much earlier. These theories are based on physically intuitive idea that due to Pauli's exclusion principle no more than two electrons are come close to each other and hence pair correlation must represent significant portion of electron correlation. In the independent electron pair approximation (IEPA) developed by both Sinanoglu[20] and Nesbet,[86] total correlation energy is represented as the sum of pair correlation energies of all possible distinct pairs of electrons. The correlation energy of each pair of electrons in two occupied orbitals is determined independently of all other pairs, by carrying out a CI doubles calculation correlating the given pair. The relation of IEPA to MBPT has been outlined in extensive reviews by Freed[93a] and Robb.[93b] The IEPA neglects coupling between pairs of electrons. A series of schemes to approximately include electron pair coupling, known as coupled electron pair approximation (CEPA), were proposed by Meyer.[87] These CEPA methods are closely related to CC method by the neglect of most of the nonlinear terms in CC equations. Unlike CC method, both IEPA and CEPA methods are not invariant with respect to separate unitary transformations among occupied and virtual orbitals. Pair correlation theories and their relation to CC method has been extensively covered in a review by Kutzelnigg.[94] Analysis of role of exclusion principle violating (EPV) terms in CEPA methods and linearized CC approximations has further led to the emergence of several sophisticated methods which continue to retain the simplicities offered by CEPA methods. The averaged coupled pair functional (ACPF) method of Gdanitz and Ahlrichs,[95] the averaged quadratic coupled-cluster (AQCC) method of Szalay and Bartlett,[96] and the self-consistent size-consistent configuration interaction (SCSC-CI) method of Daudey and Malrieu[97] are some examples of such CEPA-like methods.

Earlier CC formulations made use of spin-orbitals,[88,90] and hence are applicable to both closed-shell and open-shell situations described a single dominant UHF determinant. For situations described by a dominant closed-shell RHF determinant, such spin-orbital formulations are computationally demanding as they involve more number of cluster amplitudes than the minimum number dictated by the spin-symmetry of the targeted state. To overcome this problem, in spin-orbital CC formulations based on closed-shell RHF determinant as vacuum, a procedure known as spin-integration is usually performed by choosing an independent set of cluster amplitudes depending only on spatial orbitals and associating certain spin-integration factors to the terms in CC equations. It is known that this procedure is equivalent to spin-adaptation of CC method such that the excited configurations obtained by the action of cluster operators on RHF determinant are non-orthogonal.[25] Using the graphical methods of angular momentum for spin-adapting various cluster operators, Paldus and coworkers[25] have obtained an orthogonally spin-adapted CC formulation applicable for closed-shell states based on closed-shell RHF determinant.

Description of open-shell states usually requires multi-reference methods. However, open-shell states dominated by a single determinant are still accessible by single-reference methods. Radicals described by a single dominant UHF determinant and certain open-shell states which can be described by an high-spin ROHF determinant fall in this category. Description of such states by application of UHF or ROHF based spin-orbital CC formulations is possible, and has been carried out by several workers.[98] However, it is known to result in spin-symmetry broken solutions leading to undesirable spin-contamination of the calculated CC energies. Another major limitation which restricts the applicability of such UHF or ROHF based spin-orbital CC formulations is that the number of cluster amplitudes to be solved far exceeds the minimum number required by the spin-symmetry of the desired state.

For a proper resolution of both these problems, it is necessary to have a completely spin-adapted CC formulation for such open-shell states. In such formulations, the vacuum $|\Phi_0\rangle$ is assumed to be a proper spin-adapted configuration with a desired spin-multiplicity. The cluster operator T is expanded in terms of a minimal set of linearly independent spin-adapted excitation operators $\hat{E}_I$ as $T=\sum t_I\hat{E}_I$. These $\hat{E}_I$ are required to be constructed such that the resulting CC wave-function $e^T|\Phi_0\rangle$ is a proper eigenfunction of total spin operator $\hat{S}^2$ with the same spin-multiplicity as the vacuum. This requirement necessarily leads to construction of $\hat{E}_I$ as appropriate linear combinations of generators of underlying unitary group such that basic invariance properties of CC method under separate unitary transformations among occupied, valence and virtual orbitals are preserved. Such completely general spin-adapted CC formulations based on unitary group have been pursued by Janssen and Schaefer,[99a] Li and Paldus and coworkers,[99b,100] and Nooijen and Bartlett.[99c] Use of unitary group generators ensures that the resulting wave-function is automatically spin-adapted with minimum number of linearly independent set of cluster amplitudes. In addition, such formulations naturally allow for the use of a vacuum state constructed as a fixed linear combination of determinants which is useful to study open-shell singlet states. The major disadvantages of unitary group based CC formulations for open-shells systems is the non-commutativity of spin-adapted excitation operators. As a result, the CC energy expressions contains up to quadruple terms and CC equations contain up to octuple terms.[100]

There are several spin-adapted open-shell CC formulations based on ROHF vacuum $|\Phi_0\rangle$ where complete spin-adaptation of CC wave-function is sacrificed in favor of obtaining a simplified formulation with the same minimum number of independent cluster amplitudes. Here, spin-adapted operators $\hat{E}_I$ are constructed such that they produce proper spin-adapted configurations only when acting on vacuum $|\Phi_0\rangle$. They are not required to produce proper spin-eigenfunctions when acting on other spin-adapted configurations. In other words, the products of these spin-adapted operators are not necessarily spin-adapted. Consequently, the full CC wave-function is not a pure spin-eigenfunction and becomes so only in its linear form. Such approximate spin-adapted formulations have been pursued and extensively applied by Nakatsuji and Hirao,[101] Bartlett and coworkers,[102a,b] Szalay and Gauss,[102c] Urban and coworkers,[98] Jayatilaka and Lee,[103] and Knowles and coworkers.[104] The main advantage of these formulations is that spin-adapted operators can be constructed be commuting leading to further computational simplifications.

There are several other methods which make use of the CC ansatz for wave-function. However, determination of cluster amplitudes proceeds via some kind of stationary principle on an energy functional. They are collectively referred to as alternative or stationary CC methods. Examples include the expectation value coupled-cluster (XCC) variants of Pal and coworkers,[105-106] Bartlett and coworkers,[107] the unitary coupled-cluster (UCC) method of Kutzelnigg,[94] and the extended coupled-cluster (ECC) method of Arponen[108] extensively pursued by Pal and coworkers.[109] Although such methods are more complicated in structure as compared to the standard non-variational CC method, they are attractive due to many reasons. These methods will be discussed in detail in the sixth chapter.

I.3.8 Quasi-degeneracy and multi-reference description

The SR methods discussed in previous sub-sections are mainly applicable for the description of states dominated by a single determinant Φ_0. In quantum chemistry, such states mainly include closed-shell atomic states and near equilibrium ground states of closed-shell molecules. As discussed in previous sub-section, certain open-shell states well-described by a dominant UHF or ROHF determinant can also be studied using SR methods. A major portion of electron correlation in such states is accounted for in the mean-field description used for finding this dominant determinant. The remaining part of short range electron correlation is referred to as dynamical or external correlation. It arises due to somewhat weak interaction of various excited determinants with this dominant determinant and contributes to correlation energy of the state. It may be summarized that SR methods are suitable for description of dynamical correlation.[26]

Many situations often occur in chemistry where the state involved contains dominant contributions from several determinants.[26,30] This also indicates presence of several other states energetically nearly degenerate to the given state, and strongly interacting with it. Such a situation is known to as quasi-degeneracy. Examples of quasi-degenerate situations include general open-shell states of atoms, excited and ionized and electron attached states of atoms and molecules, reaction transition states and other regions of potential energy surfaces molecules far away from their equilibrium geometry such as in bond-dissociation processes. A quasi-degenerate state is characterized by a significant amount of non-dynamical electron correlation arising due to strong interaction between the dominant determinants. Being oriented to describe only the dynamical correlation, SR methods have often been found to fail to describe quasi-degenerate states.[30]

For proper treatment of non-dynamical correlation, it is necessary to begin by specifying a zeroth-order reference state $\Psi^{(0)}$ as an approximation to the desired quasi-degenerate state Ψ. It is usually constructed as a linear combination of a set of M strongly interacting determinants $\{\Phi_I, I = 1,\ldots,M\}$. For example, $\Psi^{(0)}$ may be obtained in an MCSCF calculation involving these determinants, but it is not necessary. It may be noted that $\Psi^{(0)}$ is not unique for a given state. Dynamical correlation is calculated using an appropriate multi-reference method and brings in a correction term X for the wave-function.

$$\begin{aligned} \Psi^{(0)} &= \sum_{I=1}^{M} C_I \Phi_I \\ \Psi &= \Psi^{(0)} + \mathrm{X} \end{aligned} \tag{1.49}$$

Methods which introduce dynamical correlation by employing such a multi-determinantal zeroth-order description are referred to as multi-reference (MR) methods.[30] They have long been recognized to be essential for proper description of quasi-degenerate states.

In most situations, the set of strongly interacting determinants $\{\Phi_I\}$ contributing to zeroth-order description of a given quasi-degenerate state is usually found to be adequate to construct zeroth-order descriptions of some of its partner quasi-degenerate states as well. In other words, the space spanned by $\{\Phi_I\}$ contains zeroth-order reference states of a manifold of quasi-degenerate states. This space is known as model space (or reference space) and is denoted by P. The space spanned by all determinants not belonging to the model space is referred to as complement space and is denoted by Q. The concept of model space is important in MR methods. It is considered as an zeroth-order approximation to the space $\mathcal{P}$ of some exact quasi-degenerate states of the full Hamiltonian $\hat{H}$ with their zeroth-order reference states in P.

Choice of model space leads to three distinct categories of underlying orbitals. The orbitals occupied in all the model space determinants are referred to as core or hole orbitals. The orbitals unoccupied in all the model space determinants are referred to as particle or virtual or excited orbitals. The orbitals which are occupied in only some of the model space determinants are referred to as active or valence orbitals. The model space determinants differ in occupancies of only valence orbitals.

In practice, model spaces are constructed in a reverse process by conveniently dividing the orbitals into core, valence and virtual categories. Using orbital energies, a zeroth-order Hamiltonian $\hat{H}_0$ is constructed so that the determinants are its eigenfunctions. A group of orbitals close to the Fermi-level with nearly degenerate orbital energies are chosen to be valence orbitals. Quasi-degeneracy is thought to arise as a consequence of near-degeneracy (with respect $\hat{H}_0$) of determinants formed when a given number of valence electrons are distributed in valence orbitals. The model space is constructed by including some of the quasi-degenerate determinants formed in this process. When all possible resulting determinants are included in the model space, it is referred to as complete model space. An incomplete model space results when only a selected subset of these determinants are included.

1.3.9 Multi-reference configuration interaction and related approaches

The multi-reference configuration interaction (MRCI)[26,110-113] method is one of the standard benchmark methods in quantum chemistry, and has been a popular tool in molecular spectroscopy for a long time. It is a straightforward extension of single-reference CI method for multi-reference situations and does not significantly differ much from it. The MRCI wave-function is constructed as a linear combinations of all distinct excited determinants generated by carrying out excitations on each determinant within the model space. Widely used is the MRCI-SD method which includes all single and double excitations with respect to each determinant in the model space.[26]

$$\Psi_{MRCI-SD} = \sum_{I=1}^{M} C_I \Phi_I + \sum_{S} C_S \Phi_S + \sum_{D} C_D \Phi_D \tag{1.50}$$

Here, Φ_S and Φ_D are respectively the singly and doubly excited determinants obtained from the set of reference functions $\{\Phi_I\}$. Since the model space usually contains singly and doubly excited determinants, the final MRCI wave-function includes some triple and quadruple excitations. As in single-reference CI method, the combining coefficients in Eq (1.50) are determined by applying the variational principle leading to diagonalization of the Hamiltonian matrix evaluated between different determinants. As mentioned earlier, modern MRCI treatments make use of spin-adapted configuration state functions (CSF) in place of determinants along with the efficient rules developed for evaluation of coupling coefficients entering the Hamiltonian matrix elements. To achieve efficiency, they further employ the direct CI method proposed by Roos[67] in combination with the graphical methods of unitarty[61-62] and symmetric group approaches.[15,68]

Since excitations from each of the model space CSFs are considered, the total number of CSFs included in MRCI wave-function scales linearly with the size of the model space. This makes it difficult to use large model spaces, especially large complete model spaces, in conventional MRCI calculations. In single-reference CI, the first-order interacting space of the reference determinant Φ_0 is spanned by all singly and doubly excited CSFs. In contrast, the excited CSFs included in MRCI expansion span a much bigger space than the first-order interacting space of the zeroth-order reference function.

Instead of generating singly and doubly excited CSFs from each of the model space CSFs, configurations may be constructed by applying excitation operators to the contracted zeroth-order reference function as a whole. Such configurations are known as internally contracted configurations (ICC).[26] As shown by Meyer,[114] the set of excited ICCs of a zeroth-order reference function span its first-order interacting space. Furthermore, the number of these excited ICCs is independent of dimension of the model space, and depend only on the number of virtual orbitals. Werner and Reinsch[115a] initiated the use of ICCs in MRCI resulting in internally contracted MRCI (ICMRCI) method. Later on, it was efficiently formulated by Knowles and Werner.[115b] The ICMRCI method allows the use of larger model spaces as compared to conventional MRCI method without introducing any significant loss of accuracy. However, these ICCs are not orthogonal and depend on the combining coefficients of model space CSFs. This complicates the evaluation of coupling constants and Hamiltonian matrix elements. For this reason, modern approaches to ICMRCI have involved a balanced combination of uncontracted CSFs and ICCs.[115b]

As with truncated CI methods, none of the MRCI methods are size-extensive. Several methods for a posteriori corrections to MRCI energy similar to Davidson correction used in single-reference CI have been proposed. On the other hand, attempts for a priori size-consistent refinements of MRCI method have lead to a number of methods which are multi-reference generalizations of the CEPA method (MR-CEPA). The MR-ACPF method of Gdanitz and Ahlrichs,[95] the MR-AQCC method of Szalay and Bartlett,[96] and the MR-SCSCCI method of Malrieu and coworkers[97,116] are some examples of such methods. All these methods are inherently state-selective and lie between MRCI and rigorously size-extensive state-selective MRCC theories. An extensive review of these methods has been presented recently by Szalay,[117] and Adamowicz and Malrieu.[118]

I.3.10 Multi-reference perturbation theory

The multi-reference perturbation theory (MRPT) approaches can be divided into two different categories.[119] The first category of approaches are based on perturbative construction of an effective Hamiltonian defined over the model space whose diagonalisation yields approximate energies and approximate wave-functions of one or more states having their zeroth-order components within the model space. They are commonly known as perurb-then-diagonalise type of approaches, and will be discussed in detail in a subsequent sub-section. For some reasons, these have been referred in the literature as quasi-degenerate perturbation theories.[29] The term MRPT is usually used for the second category of approaches which closely follow the single reference perturbation theory.[27-28] A zeroth-order wave-function $\Psi^{(0)}$ qualitatively describing the desired state Ψ is first constructed by diagonalizing the Hamiltonian over the model space, usually through an MCSCF calculation. This is then used to construct a zeroth-order Hamiltonian $\hat{H}_0$ having $\Psi^{(0)}$ as one of its eigenfunction with eigenvalue E_0. This $\hat{H}_0$ defines a perturbation $\hat{V} = \hat{H} - \hat{H}_0$. A perturbation expansion around the zeroth-order wave function is then used to calculate perturbative corrections to energies $\mathcal{E}^{(n)}$ and wave-functions $\mathrm{X}^{(n)}$ for the desired state. This approach is usually referred to as diagonalize-then-perturb approach and is inherently state-specific (one state at a time) in nature.[119]

$$\begin{aligned}
&\hat{H}_0\Psi^{(0)} = E_0\Psi^{(0)} \\
&\hat{V} = \hat{H} - \hat{H}_0 \\
&\Psi = \Psi^{(0)} + \mathrm{X} \\
&\mathrm{X} = \mathrm{X}^{(1)} + \mathrm{X}^{(2)} + \cdots \\
&\mathcal{E} = E_0 + \mathcal{E}^{(1)} + \mathcal{E}^{(1)} + \cdots
\end{aligned} \tag{1.51}$$

The basic idea of MRPT is that, since a major portion of non-dynamical correlation in the desired state has been recovered while calculating the zeroth-order wave-function, the rest is state-specific dynamical correlation which can effectively recovered in low-orders of perturbation expansion around the zeroth-order state. In practice, the MRPT approach has been employed to calculate only the first-order wave-function correction $\mathrm{X}^{(1)}$ which is sufficient to calculate energy corrections up to third-order.

A variant of second-order MRPT approach using CASSCF wave-function as zeroth-order reference function was developed[120] and successfully applied by Roos and coworkers.[27-28] It has been termed as CASPT2 method. Here, the first-order wave-function $\mathrm{X}^{(1)}$ is expanded in terms of excited ICCs. Similar approach has been taken by Wolinski and coworkers,[121] Dyall,[122] and Werner[123] in their MRPT developments. Other variants of second-order MRPT have been developed by Murphy and Messmer,[124] Hirao,[125] Kozlowski and Davidson.[126] Instead of ICCs, these variants make use of uncontracted CSFs to expand the first-order wave-function.

A main difficulty of MRPT lies in the choice of the zeroth-order Hamiltonian $\hat{H}_0$. In multi-reference cases, the zeroth-order Hamiltonian is in general non-diagonal. As a result, a set of linear equations will have to be solved to determine the first-order wave function. The issue of zeroth-order Hamiltonian in diagonalize-then-perturb type of MRPT approaches has been a subject of numerous detailed studies. This is also related to the size-consistency aspects of the method. A recent review by Andersson and Roos,[27] and recent articles by Pulay and coworkers,[127] and Malrieu and coworkers[128] contain extensive discussions on these issues.

Recent developments on MRPT have been towards achieving a balanced combination of both ICCs and uncontracted CSFs as in ICMRCI methods,[123] and the use of restricted active spaces and general MCSCF reference functions.[123,129] Implementation and applications of third-order MRPT (MRPT3 or CASPT3) has also been reported recently by Werner.[130]

I.3.11 Effective Hamiltonian approach

The effective Hamiltonian approach offers an alternative framework to develop different multi-reference methods in which a simultaneous description of a manifold of quasi-degenerate states is attempted.[29,131-132] It is based on the idea of partitioning N-electron Hilbert space into a smaller M-dimensional model space P and its complement space Q. The model space is spanned by a set of M determinants $\{\Phi_I, I = 1,\ldots,M\}$ and the complement space is spanned by $\{\Phi_I, I = M+1,\ldots,\infty\}$. In addition, the model space is assumed to be an approximation to some M-dimensional target space $\mathcal{P}$ spanned a set of M quasi-degenerate exact states $\{\Psi_A, A = 1,\ldots,M\}$ of the full Hamiltonian $\hat{H}$ with corresponding energies $\{\mathcal{E}_A, A = 1,\ldots,M\}$. This means that each quasi-degenerate state in $\mathcal{P}$ has a significant component in the model space.[25]

In effective Hamiltonian approach based methods, an operator called effective Hamiltonian H_{eff} is sought such that its eigenvalues are identical to the energies of quasi-degenerate states of $\hat{H}$ belonging to the target space $\mathcal{P}$. The corresponding eigenvectors $\{\Psi_A^{(0)}, A = 1,\ldots,M\}$ of H_{eff} within the model space represent an approximation to the corresponding quasi-degenerate states $\{\Psi_A, A = 1,\ldots,M\}$ of $\hat{H}$.

$$
\begin{aligned}
&H_{eff}\Psi_A^{(0)} = \mathcal{E}_A\Psi_A^{(0)} \quad \forall A = 1,\ldots,M \\
&\Psi_A^{(0)} = \sum_I C_{IA}\Phi_I \\
&\Psi_A = \Psi_A^{(0)} + \mathrm{X}_A
\end{aligned}
\tag{1.52}
$$

Within the model space, the H_{eff} effectively acts as if it were the full Hamiltonian $\hat{H}$, and hence the name effective Hamiltonian.[131-133] Even though H_{eff} can be defined over the entire Hilbert space, usually it is constructed such that only its matrix elements over the model space are required for the purpose of its diagonalisation to obtain $\mathcal{E}_A$ and $\Psi_A^{(0)}$. This construction proceeds by defining an operator Ω, known as wave-operator, which maps the eigenvectors of H_{eff} to the corresponding exact quasi-degenerate states in $\mathcal{P}$.

$$
\begin{aligned}
&\Omega\Psi_A^{(0)} = \Psi_A \quad \forall A \\
&\mathcal{P} = \Omega P
\end{aligned}
\tag{1.53}
$$

Two related approaches for the construction of effective Hamiltonian have been widely used in literature.[30,131-133] The first approach, referred to as similarity transformation approach, involves carrying out a similarity transformation of $\hat{H}$ by the wave-operator Ω to obtain an operator $\tilde{H}$.

$$
\tilde{H} = \Omega^{-1}\hat{H}\Omega \tag{1.54}
$$

The similarity transformation ensures that all eigenvalues of $\tilde{H}$ are same as those of $\hat{H}$. This enables $\tilde{H}$ to serve as a possible candidate for H_{eff}. The $\tilde{H}$ can be used as an H_{eff} provided a method is found to restrict the eigenvectors of $\tilde{H}$ corresponding to the quasi-degenerate states in $\mathcal{P}$ to entirely lie within the model space. In general, this is ensured by determining the wave-operator Ω in such a way that $\tilde{H}$ in some sense becomes diagonal with respect to the model space. This essentially decouples the eigenvalue equations of $\tilde{H}$ corresponding to the quasi-degenerate states in $\mathcal{P}$ from the eigenvalue equations for other states.[133] Different definitions for diagonal $\tilde{H}$ are possible, and this aspect has been examined in a review by Kutzelnigg.[83] A commonly employed definition is the minimal decoupling scheme which leads to a block triangular form for H_{eff}.

$$\begin{aligned} &Q\tilde{H}P = 0 \\ &H_{eff} = P\tilde{H}P + Q\tilde{H}Q + P\tilde{H}Q \end{aligned} \tag{1.55}$$

In the similarity transformation approach, H_{eff} is thought of as an operator within the entire Hilbert space.[133] However, only its model space component $P\tilde{H}P$ is relevant to obtain the eigenvalues and eigenvectors of desired quasi-degenerate states. In the second approach, referred to as Bloch equation approach, the Schrödinger equation for all the quasi-degenerate states in $\mathcal{P}$ is reformulated in terms of an equation involving Ω and H_{eff}. This equation is known as generalized Bloch equation[17,30,133-134] and can be written as follows.

$$\hat{H}\Omega P = \Omega H_{eff} P \tag{1.56}$$

Unlike the similarity transformation approach, matrix elements H_{eff} over only the model space enter the Bloch equation. This is a consequence of definition of H_{eff} as in Eq (1.52). The result of action of H_{eff} on the model space is the model space itself. The solution of Bloch equation proceeds by left projecting it with a complete set of states, usually P and Q. This leads to a coupled set of equations implicitly defining Ω and H_{eff}.[30]

In both these approaches, a normalization condition on Ω fixing its matrix elements over the model space i.e., $P\Omega P$ is needed. This is usually specified indirectly through parameterization of Ω. A frequently employed normalization is the intermediate normalization $P\Omega P = P$.[30,134] It means that the projections of exact the quasi-degenerates states in $\mathcal{P}$ onto P are nothing but the corresponding eigenfunctions of H_{eff} lying within the model space. In other words, when intermediate normalization is used, the action of Ω on a model space function does not generate an additional component lying within the model space.

The basic differences between these two approaches are well-known.[30,133] Similarity transformation approach is applicable only when an explicit form of the inverse of Ω is available and can be used to evaluate operator $\Omega^{-1}\hat{H}\Omega$. In this case, H_{eff} can be explicitly defined in terms of Ω. In Bloch equation approach, an explicit form of inverse of Ω is not required. However, H_{eff} now can not in general be defined as an explicit function of Ω and has to be solved in an iterative process along with Ω.[30,133] Only when intermediate normalization is used, H_{eff} can be defined in terms of Ω. Another important difference is that, in similarity transformation approach, the matrix elements of H_{eff} over the entire Hilbert space are available. They can be easily computed and used for other purposes, for e.g. to obtain other states as is done in equation-of-motion CC method. In contrast, this is not possible in Bloch equation approach as it involves the matrix elements of H_{eff} only within the model space.[133]

Effective Hamiltonians originally arose in studies on perturbation theory for degenerate states by Kato,[135a] Bloch,[135b] and des Cloizeaux.[135c-e] Since then a variety of effective Hamiltonians with different properties have been studied in literature.[131-132] The simplest and widely used effective Hamiltonian is the following one proposed by Bloch.[135b] It is obtained by imposing intermediate normalization for wave-operator in Eq (1.56).

$$\begin{aligned} H_{eff}^{Bloch} &= P\hat{H}\Omega P \\ Q\hat{H}\Omega P &= Q\Omega P\hat{H}\Omega P \end{aligned} \qquad (1.57)$$

It is well known that Bloch's effective Hamiltonian is not hermitian.[131-132] A hermitian effective Hamiltonian has been derived by des Cloizeaux[135c-e] by a transforming the right eigenvectors of Bloch's effective Hamiltonian into an orthonormal set. The relation between hermiticity of an effective Hamiltonian and norm-preserving nature of the associated wave-operator has been studied by Jorgensen and coworkers,[136] and Hurtubise and Freed.[132] Effective Hamiltonians generated by similarity transformations of the Hamiltonian in Fock-space have been extensively studied by Kutzelnigg,[83] and also by Nooijen and Meissner.[133] The energy dependent Hamiltonian appearing in the partitioning techniques of Feschbach and Lowdin, is also a kind of effective Hamiltonian.[29,131,137] The reviews by Durand and Malrieu,[131] and Hurtubise and Freed[132] contain detailed discussions on several relevant issues along with a classification and comparison of different effective Hamiltonian formulations that have appeared in the literature.

Related to effective Hamiltonians approach is the intermediate Hamiltonian approach proposed by Kirtman,[138] and Malrieu and coworkers.[131,139] Unlike effective Hamiltonians which provide exact energies of all the M quasi-degenerate states associated with the M-dimensional model space, intermediate Hamiltonians provide exact energies of only a subset of these quasi-degenerate states. Intermediate Hamiltonians are useful and flexible to avoid certain convergence problems associated with construction of effective Hamiltonians in cases where some of the targeted quasi-degenerate states do not have significant component within the model space. Malrieu and coworkers[139] have demonstrated its usefulness and efficacy in perturbative calculations.

Mukherjee and coworkers,[140] and Meissner and coworkers[133,141] have extensively used intermediate Hamiltonian approach to formulate non-perturbative coupled-cluster schemes.

The effective Hamiltonian approach provides a theoretical framework in which both perturbative as well as non-perturbative schemes for computation Ω and H_{eff} can be formulated. While perturbative schemes lead to quasi-degenerate perturbation theory, non-perturbative ones mainly result in multi-reference coupled-cluster methods.

I.3.12 Quasi-degenerate perturbation theory

Unlike MRPT where perturbation expansion is carried out for a single quasi-degenerate state around a zeroth-order reference state, the basic idea of quasi-degenerate perturbation theory (QDPT) is to carry out a perturbation expansion of the entire quasi-degenerate target space $\mathcal{P}$ around the model space P.[17,29] As in single-reference perturbation theory, the Hamiltonian $\hat{H}$ is separated into a zeroth-order Hamiltonian $\hat{H}_0$ and a small perturbation $\hat{V}$. The zeroth-order Hamiltonian is constructed such that the model space P and the complementary space Q are its eigen subspaces. It is further assumed that P and Q are energetically well separated with respect to $\hat{H}_0$, and that the model space provides a zeroth-order approximation for the target space. Usually, $\hat{H}_0$ is constructed such that determinants in P and Q are its eigenfunctions.[17,29] Under these conditions, the complementary space weakly interacts with the model space through the perturbation $\hat{V}$, and perturbation expansion is well-defined. In the framework of effective Hamiltonian theory, such a perturbation expansion is carried out for the wave-operator Ω and the effective Hamiltonian H_{eff}.

$$\begin{aligned} \Omega &= \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} + \cdots \\ H_{eff} &= H_0 + H_{eff}^{(1)} + H_{eff}^{(2)} + \cdots \end{aligned} \tag{1.58}$$

Different versions of QDPT mainly differ in the form used for effective Hamiltonian and wave-operator, and provide different expressions for determining individual terms in the above series expansion. Using $\hat{H} = \hat{H}_0 + \hat{V}$ for Bloch's effective Hamiltonian in Eq (1.57) leads to the following equation, referred to as generalized Bloch equation.[17,29]

$$\begin{aligned} &[\Omega, \hat{H}_0]P = V\Omega P - \Omega P V \Omega P \\ &H_{eff}^{Bloch} = PH_0P + PV\Omega P \end{aligned} \tag{1.59}$$

This equation is a generalization of the equation for Ω and H_{eff}^{Bloch} derived by Bloch[135b] for degenerate model spaces, to the case of general quasi-degenerate model spaces. Substituting Eq (1.58) in the above equation leads to expressions for $\Omega^{(n)}$ in terms of lower-order quantities.[17,29]

$$\begin{aligned} &[\Omega^{(n)}, \hat{H}_0]P = V\Omega^{(n-1)}P - \sum_{m=1}^{n-1} \Omega^{(n-m)} P V \Omega^{(m-1)} P \\ &\Omega^{(0)} = 1 \end{aligned} \tag{1.60}$$

The above equation is used as a basis to generate order-by-order many-body Rayleigh-Schrödinger (RS) perturbative expansion for determination of Bloch's effective Hamiltonian and wave-operator. Such an expansion was first carried out by Brandow[142] by using a diagrammatic representation for the above equations. For a complete degenerate model space, Brandow proved that unlinked diagrams present in any order of RS expressions for wave-operator and effective Hamiltonian cancel in each other exactly. To achieve this, Brandow introduced the concept of folded diagrams. Later on, Lindgren extended Brandow's results to complete quasi-degenerate model spaces.[17,143] This essentially generalizes the non-degenerate version of linked diagram theorem of

Goldstone[84a] and Hugenholtz,[84b] to quasi-degenerate systems described by Bloch's effective Hamiltonian in a complete model space. In this case, the Effective Hamiltonian is represented by connected diagrams and the wave-operators is represented by linked diagrams. This reflects the size-extensivity of Bloch's effective Hamiltonian for complete model spaces.

QDPT formulations leading to hermitian effective Hamiltonians have been extensively pursued by several workers, including Kato,[135a] des Cloizeaux,[135c-e] Brandow,[142a] Klien,[144] Jorgensen and coworkers,[136] Kvasanicka,[145] Freed and coworkers,[132,146] Westhaus and coworkers,[147] Suzuki,[148a] Bartlett and Redmon,[148b] Shavitt and Redmon,[149] Kirtman,[150a,b] Certain and Hirschfelder,[150c,d] Haque and Mukherjee[151]. Shavitt and Redmon[149] developed generalization of Eq (1.60) applicable to different versions of QDPT formulations. Different versions of QDPT are characterized by different requirements on the diagonal part of the wave-operator.[29]

Use of complete model spaces is often fraught with convergence difficulties due to the intruder state problem.[152] Intruder states are functions from the complement space which have energies within the range of energies of target states, and cause divergences in perturbation expansion. It is well-known that this is mainly caused by energetically high-lying model space functions.[29,152] Convergence difficulties can be overcome by moving such functions into the complementary space. However, such a model space is in general, an incomplete model space. Use of such incomplete model spaces in QDPT was first suggested by Hose and Kaldor,[153] who derived diagrammatic expressions for the resulting expansion. Their diagrammatic formulation of QDPT differed from earlier formulations by using different model space determinants as vacuums. Incomplete model spaces containing valence holes as well as valence particles were used by Brandow,[154] Lindgren,[155] and Haque and Mukherjee[151] in their QDPT formulations.

The proof of linked diagram theorem was only known for the case of complete model spaces. Disconnected diagrams entering effective Hamiltonian expressions in such incomplete model space based QDPT formulations indicated the loss of size-extensivity feature, and this can be attributed to the absence of an underlying linked diagram theorem. Later on, Mukherjee,[156] working on multi-reference coupled-cluster formulations using incomplete model spaces, traced these size-extensivity difficulties to the use of intermediate normalization condition on wave-operator. This was shown to be incompatible with size-extensivity requirements for effective Hamiltonian formulations based on incomplete model spaces. By using alternative normalization conditions which lead to linked diagram theorem, Mukherjee and coworkers[157] obtained size-extensive QDPT formulations. Meissner and coworkers[158] extended these results to incomplete model space based QDPT formulation of Hose and Kaldor.

First molecular application of Brandow's version of QDPT was carried out by Kaldor.[159] Several successful applications of QDPT formulation involving a hermitian valence-shell effective Hamiltonian have been carried out by Freed and coworkers.[146] Nakano has formulated and successfully applied a version of QDPT where a set of MCSCF reference-functions are used to define the model space. The incomplete model space based QDPT version of Hose and Kaldor has also found some applications.[161] A review and a recent article by Hoffmann[29] extensively discuss different QDPT formulations and their applications.

I.3.13 Multi-reference coupled-cluster theory

In contrast to the SRCC theory which mainly evolved from its correspondence with the single reference MBPT, the evolution of multi-reference coupled-cluster (MRCC) theories has been more or less independent of the underlying perturbative structure. An MRCC theory is obtained by finding an exponentially parameterized ansatz for the wave-operator Ω, and formulating a scheme for unambiguous determination of these parameters. The latter requirement leads to casting MRCC theory within an effective Hamiltonian framework. The motivation for exponential parameterization comes from the possibility of obtaining size-extensive results, along with the usual high accuracy stemming from partial infinite-order summation nature of CC theory.

Unlike in SRCC where there is only one way to parameterize, several possibilities open up for the multi-reference case.[25,30,134] Initial formulations of MRCC theories used complete model spaces (CMS). With such model spaces, it is easy to exponentially parameterize Ω to satisfy intermediate normalization, and also to prove size-extensivity of the resulting MRCC theory. Mainly two different classes of ansatz have been used. The first one, proposed by Jezioroski and Monkhorst,[162] is referred to as state-universal or Hilbert-space ansatz. It introduces a cluster operator for each model space determinant. The wave-operator is written as follows.

$$\Omega = \sum_I e^{T_I} \mid \Phi_I \rangle\langle \Phi_I \mid \tag{1.61}$$

Here, T_I is the cluster operator associated with model space determinant Φ_I. When expressed in second-quantization notation by taking Φ_I as hole-particle vacuum, T_I is similar in structure to the SRCC cluster operator T as in Eq (1.35). T_I contains all hole-particle excitations out of vacuum Φ_I. To enforce intermediate normalization, the cluster amplitudes in T_μ corresponding to the excitations leading to states within model space, are explicitly set to zero.[162]

It is well-known that the wave-operator Ω in Eq (1.61) is not invertible within the Hilbert-space containing same number of electrons as the model space determinants.[162] Therefore, similarity transformation approach to obtain effective Hamiltonian is not possible. Bloch equation method leads to standard equations of state-universal MRCC theory, and will be described in detail in the second chapter. This method is suited to study potential energy surfaces of molecules.

Search for an invertible exponentially parameterized ansatz expressed in second quantization form around a single hole-particle vacuum Φ_0 leads to several possibilities.[17,25,30,134,143b,163-167] It is known that it is not possible to obtain an invertible ansatz with unambiguously defined cluster amplitudes by staying within the Hilbert space containing the same number of electrons as the model space determinants.[134,167] Resolution of ambiguities or redundancies in the definition of the cluster operator inevitably leads to use of so called valence-universal strategy or Fock-space strategy.[30,167] All MRCC theories adapting this strategy are referred to as valence-universal MRCC (VUMRCC) or Fock-space MRCC (FSMRCC).

There are two variants of VUMRCC depending on the type of model spaces employed. Choice of the vacuum Φ_0 divides the set of orbitals into holes and particles. Selection of the model space further divides the hole orbitals into occupied or core orbitals and valence-hole orbitals. Similarly, the particle orbitals are divided into unoccupied or virtual particles and valence-particle orbitals. With the hole-particle picture, a determinant in the model space contains certain number of valence-holes and valence-particles. Therefore, model space, in general, contain determinants with different number of valences-holes and valence-particles.[30,134]

In the first variant, known as valence-particle (or valence-hole) VUMRCC, the model space and vacuum is chosen such that all the model space determinants contain only valence-particles (or only valence-holes). Since the model space belongs of the Hilbert space with a fixed number of electrons N, all the model space determinants in the first variant of MRCC contain a fixed number n_p of valence-particles (or a fixed number n_h of valence-holes in case of valence-hole VUMRCC). The model space is known as n_p-valence particle (or n_h-valence hole) model space. Usually, this model space is generated by distributing n_p valence-particles into n_v number of valence orbitals. A complete n_p-valence model space results when all possible determinants obtained in such a distribution are included. Otherwise, this n_p-valence model space is incomplete.[30,134]

The second variant, known as valence hole-particle VUMRCC, employs a model space containing both valence-holes and valence-particles. Again, since the model space belongs of the Hilbert space with a fixed number of electrons N, all the model space determinants in the second variant must contain a fixed difference $(n_p - n_h)$ of valence-holes and valence-particles. In general, such a model space is incomplete.

Use of valence-universal strategy in a general case means that the wave-operator Ω correlating the chosen model space (parent model space) also correlates all distinct spaces formed by determinants obtained by systematically deleting the valence holes and the valence particles in all possible ways from the parent model space determinants.[134] This procedure is referred to as subduction and resulting spaces are referred as subduced model spaces. Hence, a valence-universal Ω not only correlates parent model space but also all subduced model spaces formed during subduction procedure.[30,134] Consequently

H_{eff} is also a valence-universal operator which upon action of subduced model spaces provides correlated energies of subduced systems.

As pointed out earlier, a model space containing both valence holes and valence particles is in general an incomplete model space (IMS). Since achievement of size-extensivity was not possible with IMS, initial developments of VUMRCC used complete n-valence particle model spaces. The determinant with only core orbitals is taken as hole-particle vacuum. With this choice of vacuum, parent model space $P^{[n]} = P$ now contains determinants with a fixed number n of valence particles. The subduced model spaces $P^{[i]}, i = (n-1), \ldots, 0$ contain determinants with i valence particles and are obtained by deleting $(n-i)$ valence particles from the parent model space. A valence-universal exponential ansatz mapping the model spaces $\left\{P^{[i]}, i = 0, \ldots, n\right\}$ into the corresponding exact spaces $\left\{\mathcal{P}^{[i]}, i = 0, \ldots, n\right\}$ has been proposed by Mukherjee and coworkers.[163]

$$\begin{aligned} &\Omega = e^{T} \\ &T = \sum_{i=0}^{n} T^{[i]} \end{aligned} \tag{1.62}$$

Here, T is the cluster-operator defined with respect to the hole-particle vacuum Φ. In addition to the cluster operator $T^{[0]}$ similar to the SRCC cluster operator inducing hole-particle excitations from Φ_0, it also includes operators $T^{[i]}, i = 1, \ldots n$ inducing hole-particle excitations from $P^{[i]}$. The cluster operators $T^{[i]}$ have exactly i annihilation operators corresponding to valence particles ($T^{[i]}$ is said to be of valence rank i). As a consequence they do not commute. Intermediate normalization is achieved by excluding from T, the operators inducing hole-particle excitations within the model spaces. It is known that use of such non-commutable entities within the cluster operator of a single exponential leads to fully coupled set of equations for different i-valence cluster amplitudes.[30,163]

As shown by Mukherjee and coworkers,[163c-d,] a partial hierarchical decoupling referred to as Subsystem Embedding Condition (SEC) can be enforced by using an ansatz containing a product of exponentials in which cluster operator within each exponential include only operators of a particular valence particle rank. Even though decoupling of equations is obtained in this approach, this does not simplify the non-commutativity problem. A solution to non-commuting cluster operators is possible by using Lindgren's normal-ordered exponential ansatz.[17,25,30,134,143b,163e,167]

$$\Omega = \left\{ e^{T} \right\} \qquad (1.63)$$

Here, square braces denote the normal-ordering with respect to the vacuum Φ_0 and T has the same decomposition as in Eq (1.62). Due to normal-ordering, contraction between different cluster operators within the exponential is avoided thereby simplifying the resultant equations. The explicit form of inverse of normal ordered exponential is not known. Therefore, Bloch equation approach is the only approach that can be followed to obtain the cluster amplitude equations. It has been shown that this leads to a connected set equations for each valence sectors and SEC emerges naturally as consequence of normal-ordered form of ansatz. Because of these simplifications, the normal-ordered exponential ansatz has become the standard ansatz for VUMRCC theories and their applications.

As mentioned in the previous subsection, the CMS are usually fraught with convergence and instability problems due to the intruder state problem. Following suggestion by Hose and Kaldor in QDPT, several workers have used IMS (particularly IMS containing both valence-holes and valence-particles) based MRCC formulations.

However, it was generally believed that size-extensivity was not possible for such IMS based theories. Size-extensive MRCC theories based on general IMS were made possible by certain important results of Mukherjee[156] on the non-suitability of intermediate normalization for such model spaces. Later on Lindgren and Mukherjee,[134] and Kutzelnigg and coworkers[168] have clearly demonstrated necessary and sufficient conditions for connectivity in various VUMRCC theories. The main conclusions of their analysis is (i) valence-universality of Ω and H_{eff} is necessary, but not sufficient for connectivity (ii) valence-universality is incompatible with intermediate normalization when incomplete model spaces are used. Mukherjee has shown that,[156b] by dropping the requirement of intermediate normalization and by adopting valence-universal Ω and H_{eff} along with additional conditions for partitioning closed-components of $T^{[i]}$ and $H_{eff}^{[i]}$, size-extensive VUMRCC theories for general incomplete model spaces can be obtained.

Similar conclusions can been reached for an IMS containing both valence holes and valence particles. Such model spaces are known to be suitable for calculation of difference energies of chemical interest such as ionization potentials, electron affinities and excitation energies. Most interesting among such model spaces the special ones obtained by distributing fixed number n_h of valence holes and n_p valence particles in all possible ways, separately among the chosen valence hole orbitals and valence particle orbitals respectively. They are referred to as quasi-complete model spaces (QCMS).[155] These model spaces have a number of properties similar to that of CMS, such as distinction of closed and open operators through their orbital labels. These properties allow the use of familiar diagrammatic treatment of algebraic equations with minimal book-keeping. Furthermore, for such model spaces valence-universality is particularly simple to achieve without introducing any extra set of closed cluster operators as is necessary in general IMS. Because of all such special properties, it is not surprising that most of the applications of VUMRCC theory for excitation energies till date have been based on QCMS.

Several applications of VUMRCC have been reported in the literature.[169-172] Although VUMRCC can in principle be applied for the calculation of energies of individual states, its most practical applications have been for computation of spectroscopic difference energies such as ionization potentials, electron affinities, and excitation energies of an underlying closed shell vacuum. Calculations of ionization potentials, electron affinities, and excitation energies have been based on one valence-hole CMS $P^{[0,1]}$, one valence-particle CMS $P^{[1,0]}$, and one valence particle-hole QCMS model space $P^{[1,1]}$, respectively.[169-171] Higher valence particle-hole complete and quasi-complete Fock-space sectors have also been of pursued.[173]

Historically, three apparently different variants of VUMRCC were independently developed by Mukherjee and coworkers,[163] and Offerman and coworkers,[164] and Lindgren.[17,143b,155] Mukherjee and coworkers worked with the non-commuting ansatz Eq (1.62) and its variants enforcing partial decoupling, and used similarity transformation approach to obtain the cluster amplitude equations. Offerman[164] and coworkers worked with a scheme to hierarchically build the valence-universal wave-operator by solving Bloch equations corresponding to systems with increasing number of valence particles, starting from the vacuum with no valence particles. Lindgren[143b] derived the normal-ordered ansatz along with corresponding equations for cluster amplitudes though an analysis Brandow's linked diagram theorem for QDPT.[142] Kutzelnigg and coworkers, and Stolarczyk and Monkhorst proposed MRCC theories based on diagonalizing similarity transformations in Fock-space. The reviews by Lindgren and Mukherjee,[134] and

Mukherjee and Pal,[30] and Paldus,[25] and the article by Jezioroski and Paldus,[167] serve clarify the connections between these different MRCC formulations. Recent VUMRCC formulations by Meissner,[174] and Nooijen[175] have involved generating Fock-space similarity transformations of the Hamiltonian using normal-ordered exponential to generate effective and intermediate Hamiltonians.[133]

The VUMRCC theory for one valence-hole and one valence-particle Fock-space sectors is closely related to several other single reference based methods mainly used for direct calculation of energy differences. The coupled-cluster linear response (CCLR),[176-179] equation-of-motion CC (EOM-CC),[180] similarity transformed equation-of-motion CC (STEOM-CC),[181] and symmetry-adapted cluster CI (SAC-CI)[182] are some examples of such methods. This relationship has been extensively discussed by Meissner and coworkers,[183] Mukherjee and coworkers,[184] and Nooijen and coworkers.[181c]

I.4 Atomic and molecular properties

Although stationary state electronic energies are important in spectroscopy of atoms and molecules, one is often interested in subsequent computation of various non-energetic properties.[3] According to the postulates of quantum mechanics, wavefunction contains all information about the system, and all other properties of the system can in principle be extracted using it.[1] In quantum mechanics, a property a of a system in state Ψ is the expectation value of a corresponding property operator $\hat{A}$.

$$a = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{1.64}$$

Molecular properties such as dipole moment can be computed using this approach. However, there are several other molecular properties such as, polarizabilities, transition moments, which can not be expressed as expectation value of a property operator as in Eq (1.64). For example, polarizability is related to the dipole moment induced when molecule is placed in an external electric field. Such molecular properties are a measure of how a molecule responds (as indicated by change in a molecular observable such as dipole moment) to some external field, and are referred to as response properties.[3,33a,45] To define these properties, the Hellmann-Feynman theorem (HFT) can be used.[3] This theorem relates the first derivative of energy with respect to a parameter p in the Hamiltonian $\hat{H}(p)$ to the expectation value of an operator obtained by differentiating the Hamiltonian with respect to p.

$$\frac{\partial E(p)}{\partial p} = \frac{\langle \Psi(p) | \frac{\partial \hat{H}(p)}{\partial p} \hat{A} | \Psi(p) \rangle}{\langle \Psi(p) | \Psi(p) \rangle} \tag{1.65}$$

Here, $\Psi(p)$ is an exact eigenvector of $\hat{H}(p)$. For defining static molecular electric polarizabilities, an interaction term $\hat{H}^{(1)} = -\vec{d} \bullet \vec{F}$ representing interaction of molecule dipole moment $\vec{d}$ with a constant external electric field $\vec{F}$ is added to the molecular Hamiltonian $\hat{H}$.

$$\hat{H}(\vec{F}) = \hat{H} - \vec{d} \bullet \vec{F} = \hat{H} - \sum_{i=1}^{3} d_i F_i \tag{1.66}$$

Application of HFT by treating different components of the constant applied electric field as parameters of Hamiltonian leads to expression for expectation value of i-th component of dipole moment of a molecule in presence of electric field $\vec{F}$ as follows.

$$d_i(\vec{F}) = -\frac{\partial E(\vec{F})}{dF_i} \tag{1.67}$$

The applied field is considered to be weak so that interaction $\hat{H}^{(1)}$ may be small enough to permit application of time-independent perturbation theory. This in turn permits the use of Taylor series expansion for $E(\hat{F})$ in Eq (1.67) around the zero-field strength. It is known that this procedure leads to identify various molecular electric polarizabilities as higher-order derivatives of molecular energy with respect to different components of the electric field, evaluated at zero-field strength.[3,33a,45] The permanent dipole moment can be reinterpreted as first-order energy derivative. Although HFT is applicable for exact molecular eigenstates and some categories of variationally optimized molecular wavefunctions, even for approximate wavefunctions, different response properties may still be identified as derivatives of molecular energy with respect to field strength parameters of an external applied field.

Consideration of electric field perturbation leads to molecular electric response properties, and geometric perturbations lead to identification of molecular energy gradients and hessians as some kind of response properties. Application of different kind of perturbations leads to identification of different kind of molecular response properties.[3,45]

For defining properties such as frequency-dependent polarizability, a time-dependent weak perturbation needs to be considered.[45] This requires the use of time-dependent perturbation theory, whose results are often expressed in terms of some fundamental quantities known as response functions. Therefore, it is referred to as time-dependent response approach.[45] These response functions contain information about time development of expectation values of system operators. The advantage of using response functions is that they determine various kinds of properties. The linear, quadratic and cubic response functions can be used to determine frequency dependent polarizabilities, hyperpolarizabilities and second hyperpolarizabilities. The poles and residues of response functions determine various excitation and transition properties.[45] Therefore, the task of computing different molecular properties reduces to computation of various response functions, which can be shown obey well-defined hierarchical equations of motion.[45]

The response approach provides a general conceptual and computational framework to study and compute different molecular properties. Its potential to unify a wide range of molecular properties within a single framework becomes fully visible in its time-dependent form. However, in this thesis, we will be mainly concerned with static molecular response properties. For this purpose, the time-dependent response approach need not be applied in its full generality. Instead, its static version involving simple Taylor series expansion, is sufficient for our purposes. This simply involves evaluating certain derivatives (using finite-difference and analytic approaches) of molecular energy with respect to an external perturbation field strength parameter. In turn, this requires evaluation of derivatives of molecular wavefunction parameters with respect to the external field strength parameter.

I.5 Computation of molecular properties in SRCC theory

A computational framework to analytically calculate various properties in SRCC theory was first outlined by Monkhorst[176] using response approach. A small time-independent perturbation, $\hat{H}^{(1)} = g\hat{O}$, linear in strength parameter g, is added to the molecular Hamiltonian $\hat{H}$.

$$\hat{H}(g) = \hat{H} + g\hat{O} \tag{1.68}$$

With this, SRCC energy $\mathcal{E}$ and cluster amplitudes T become functions of strength parameter g, and are denoted by $\mathcal{E}(g)$ and $T(g)$ respectively. Inserting Eq (1.68) into SRCC equations Eq (1.42)-(1.43), and expanding $\mathcal{E}(g)$ and $T(g)$ using a Taylor series around zero perturbation strength $g=0$, and collecting terms of same order in g, expressions for various derivatives of SRCC energy (molecular properties) can be obtained.[33a,176] For the first order, neglecting orbital response, the following equations are obtained.[33a,40]

$$\mathcal{E}^{(1)} = Y^T \bullet T^{(1)} + Q(\hat{O}) \tag{1.69}$$

$$AT^{(1)} = B(\hat{O}) \tag{1.70}$$

$$AT^{(1)} = \left\{ \sum_i \langle \Phi_q | e^{-T} [\hat{H}, \tau_i] e^T | \Phi_0 \rangle t_i^{(1)}, \quad \forall \Phi_q \right\} \tag{1.71}$$

$$Y^T T^{(1)} = \sum_i \langle \Phi_0 | e^{-T} [\hat{H}, \tau_i] e^T | \Phi_0 \rangle t_i^{(1)} \tag{1.72}$$

$$B(\hat{O}) = \left\{ \langle \Phi_q | e^{-T} \hat{O} e^T | \Phi_0 \rangle, \quad \forall \Phi_q \right\} \tag{1.73}$$

$$Q(\hat{O}) = \langle \Phi_0 | e^{-T} \hat{O} e^T | \Phi_0 \rangle \tag{1.74}$$

In the above equations, $T^{(1)}$ is the first derivative of the cluster amplitude, and $t_i^{(1)}$ is the specific cluster amplitude associated with the excitation operator τ_i. The terms within braces in Eq (1.71) and (1.73) form column vectors, and superscript on Y^T denotes transpose. The Eq (1.69) clearly shows that first-order response of cluster amplitudes $T^{(1)}$ is required for calculating first derivative of energy $\mathcal{E}^{(1)}$. This is obtained by solving the linear equation presented in Eq (1.70). This needs to be solved for every mode of perturbation, which is a clear disadvantage. This disadvantage arises due to the fact that SRCC theory is non-variational (or non-stationary) theory, and it does not have advantages of generalized Hellmann-Feynman theorem and $(2n+1)$-rule of variational theories.[37]

A step towards eliminating this apparent disadvantage of SRCC theory was taken by Bartlett and coworkers[39,40,42] using the idea of algebraic Z-vector technique introduced by Handy and Schaefer[38] in their analysis of analytic derivatives for CI method. By inverting Eq (1.70) and substituting it into Eq (1.69), $\mathcal{E}^{(1)}$ can be rewritten as follows.

$$\mathcal{E}^{(1)} = Z^T \bullet B(\hat{O}) + Q(\hat{O}) \tag{1.75}$$

$$Z^T A = Y^T \tag{1.76}$$

The Eq (1.76) is a perturbation independent linear equation, whose solution yields the Z-vector. The advantage of such a reorganization is, unlike earlier Eq (1.70) which needs to be solved for every mode of perturbation, equation (1.76) is perturbation independent and needs to solved only once. The Z-vector method is in some sense an analogue of generalized Hellmann-Feynman theorem for non-stationary methods. Further simplifications in Eq (1.75)-(1.76) can be carried out by introducing effective SRCC density matrices much akin to CI derivative developments.[42] The technique of Rice and coworkers can also be applied to reduce the number of AO to MO transformations.[41,184] First applications of CC analytic derivatives have been reported by Bartlett and coworkers[186] and Scheiner and coworkers.[187]

The conceptually simple procedure of eliminating $T^{(1)}$ in favor of a perturbation independent Z-vector is somewhat cumbersome for higher-order properties, and has been pursued by Salter and coworkers. However, Jorgensen and coworkers[41,43-44] have pursued an attractive alternative formulation of SRCC derivatives which automatically incorporates the benefits of Z-vector technique to all orders. This approach, known as constrained variation approach, involves construction of a functional with undetermined Lagrange multipliers λ_q corresponding to SRCC equations as follows.

$$\mathcal{J}(\Theta) = \langle \Phi_0 | e^{-T} \hat{H} e^{T} | \Phi_0 \rangle + \sum_{q \neq 0} \lambda_q \langle \Phi_q | e^{-T} \hat{H} e^{T} | \Phi_0 \rangle \qquad (1.77)$$

Optimization of the above functional leads to the same equations as SRCC equations and Z-vector equations Eq (1.76), with $\Lambda = \{\lambda_q, \forall q\}$ taking the role of the Z-vector. In this formulation, it is transparent to derive expressions for higher order derivatives. While the cluster amplitude derivatives obey the $(2n+1)$-rule, the derivatives of Lagrange multipliers obey $(2n+2)$-rule.[44] Koch and coworkers have used this approach to obtain efficient expressions for up to third-order molecular properties.[44]

I.6 Molecular properties using MRCC theories

Application of response approach to obtain molecular properties using effective Hamiltonian based MRCC theories was initiated by Pal,[46a] who, following the approach of Monkhorst in SRCC,[176] outlined the formulation for the effective Hamiltonian based MRCC theory. Specific expressions were obtained for one valence-hole, one valence-particle, and one valence hole-particle sectors of VUMRCC theory.[46b] Its applications to compute first-order molecular properties such as dipole-moments of open-shell radicals and excited states of several molecules have been carried out in recent years.[47] Ajitha and Pal have suitably extended the formulation to enable calculation of frequency-dependent properties.[48]

The above developments do not include the Z-vector method. Recently, Ajitha and Pal[55] have attempted to extend the Z-vector method to VUMRCC theory. However, their attempt has not been completely successful. Working on VUMRCC response equations for the one valence-hole sector, they have concluded that only the highest sector cluster amplitude first derivatives can be eliminated from the first derivative expressions of effective Hamiltonian under certain assumptions on the form the effective Hamiltonian.

A constrained variation approach along the lines of Jorgensen and coworkers[41] has been recently used by Szalay[49] to estimate the relative cost of MRCC first-order response calculations as compared to SRCC response equations. This is done by constructing a functional with Lagrange multipliers, for a specific state in the manifold which yields MRCC cluster amplitude equations, along with effective Hamiltonian diagonalisation equations.

I.7 Objectives and scope of the thesis

An extension of various theoretical and computational developments in SRCC response approach which enabled it to be suitable for routine use has not been studied in detail MRCC theories. The relationship of between the algebraic Handy-Schaefer Z-vector approach and the constrained variation approach for these MRCC theories followed by Szalay,[49] also needs to be clarified.

In this thesis, we plan to undertake a systematic study to extend the various concepts and issues that arose in SRCC response developments to effective Hamiltonian based MRCC theories. In particular, we intend to extend the SRCC Z-vector approach to MRCC theories, and study its relation to the state-dependent constrained variation approach. This is further pursued to obtain efficient expressions up to third-order properties using MRCC theories. Both complete and incomplete model space based MRCC theories are included in our developments, and this extends the applicability of the results. Such developments are essential to initiate routine applications of MRCC theories for the calculation of molecular properties.

In the second chapter, we formulate an analytic response approach for computation of first-order molecular properties using state-universal MRCC theory. We study the resulting response equations, and suitably generalize the SRCC Z-vector method and associated concepts to state-universal MRCC response theory.

In the third chapter, we propose a state-dependent constrained variation approach for state-universal MRCC theory, which includes the Z-vector developments of second chapter as a zeroth-order result. Certain degree of freedom in the choice of the functional is observed. The method is then applied to derive generic efficient expressions up to third-order molecular properties in state-universal MRCC.

In the fourth chapter, a pilot application of the above developments to compute dipole-moment curves of ground and three low-lying excited states of HF molecule using complete model space based state-universal MRCC theory is reported.

In the fifth chapter, a generalization of constrained variation procedure to incomplete model space based MRCC theories is formulated. This is then applied to derive generic expressions for up to third-order molecular properties in valence-universal MRCC. Diagrammatic expressions for Lagrange multiplier equations are derived for one valence-hole, one valence-particle, and one valence hole-particle valence-universal MRCC theories.

In the sixth chapter, we explore possibilities of a size-extensive, stationary, state-specific MRCC theory which suitably generalizes the single reference ECC theory[108-109] to multi-reference situations. The constrained variation approach is used as a starting point to derive such theories.

References

1. I. N. Levine, *Quantum Chemistry*, (IV Edition, Prentice Hall, New Delhi, 1995)
2. A. Szabo, and N. S. Ostlund, *Modern Quantum Chemistry*, (McGraw-Hill, New York, 1989)
3. P. W. Atkins, *Molecular Quantum Mechanics*, Volume I & II, (Clarendon, Oxford, 1970)
4. A. C. Hurley, *Electron Correlation in Small Molecules*, (Academic, London, 1976)
5. *Modern Theoretical Chemistry*, Volume 3 & 4, Edited by H. F. Schaefer III, (Plenum, New York, 1977)
6. *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, Edited by C. E. Dykstra, (Reidel, Dordrecht, 1984)
7. *Methods in Computational Chemistry*, Volume 1, Edited by S. Wilson (Plenum, New York, 1987)
8. *Ab Initio Methods in Quantum Chemistry*, Part I & II, Edited by K. P. Lawley, Advances in Chemical Physics series, Volume LXVII and LXIX, (Wiley, New York, 1987)
9. *Methods in Computational Molecular Physics*, Edited by S. Wilson and G. H. F. Dierksen, (NATO ASI Series B: Physics, Volume 293, Plenum, New York, 1992)
10. *Modern Electronic Structure Theory*, Part I and II, Edited by D. R. Yarkony, (Advanced Series in Physical Chemistry, Volume 2, World Scientific, Singapore, 1995)
11. *Modern Methods and Algorithms of Quantum Chemistry*, Proceedings, Second Edition, Edited by J. Grotendorst, (Neumann Institute of Computing Series, Volume 3, Julich, 2000)

12. J. Simons, *An Introduction to Theoretical Chemistry*, (Cambridge University Press, 2003)
13. P. O. Lowdin, Adv. Chem. Phys. **2**, 207 (1959)
14. I. Shavitt, in *Methods of Electronic Structure Theory*, Edited by H. F. Schaefer III, (Plenum, New York, 1977), p189
15. J. Karwowski, in *Methods in Computational Molecular Physics*, Edited by S. Wilson and G. H. F. Dierksen, (NATO ASI Series B: Physics, Volume 293, Plenum, New York, 1992), p65
16. S. Raimes, *Many-Electron Theory*, (North-Holland, Amsterdam, 1972)
17. I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, (Springer-Verlag, Berlin, 1982)
18. R. Manne, Int. J. Quant. Chem. **S11**, 175 (1977)
19. F. E. Harris, H. J. Monkhorst, and D. L. Freeman, *Algebraic and Diagrammatic Methods in Many-Fermion Theory*, (Oxford Press, New York, 1992)
20. (a) O. Sinanoglu, J. Chem. Phys. **36**, 706 (1961) (b) ibid, Adv. Chem. Phys, **6**, 315 (1964)
21. (a) J. Cizek, J. Chem. Phys. **45**, 4256 (1966) (b) J. Cizek, Adv. Chem. Phys. **14**, 35 (1969) (c) J. Cizek and J. Paldus, Int. J. Quantum Chem. **5**, 359 (1971)
22. (a) R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981) (b) ibid, J. Phys. Chem. **93**, 1697 (1989) (c) R. J. Bartlett, in *Modern Electronic Structure Theory*, Part II, Edited by D. R. Yarkony, (Advanced Series in Physical Chemistry, Volume 2, World Scientific, Singapore, 1995), p1047
23. M. R. Hoffmann and H. F. Schaefer, Adv. Quant. Chem. **18**, 207 (1986)
24. S. A. Kucharski and R. J. Bartlett, Adv. Quant. Chem. **18**, 281 (1986)

25. J. Paldus, in *Methods in Computational Molecular Physics*, Edited by S. Wilson and G. H. F. Dierksen, (NATO ASI Series B: Physics, Volume 293, Plenum, New York, 1992), p99
26. P. Knowles, M. Schutz, and H. J. Werner in *Modern Methods and Algorithms of Quantum Chemistry*, Proceedings, Second Edition, Edited by J. Grotendorst, (Neumann Institute of Computing Series, Volume 3, Julich, 2000)
27. K. Andersson and B. O. Roos, in *Modern Electronic Structure Theory*, Part I, Edited by D. R. Yarkony, (Advanced Series in Physical Chemistry, Volume 2, World Scientific, Singapore, 1995), p55
28. B. O. Roos, K. Andersson, M. P. Fulscher, P. A. Malmqvist, L. S. Andres, K. Pierloot, and M. Merchan, Adv. Chem. Phys. **93**, 219 (1996)
29. M. R. Hoffmann, in *Modern Electronic Structure Theory*, Part II, Edited by D. R. Yarkony, (Advanced Series in Physical Chemistry, Volume 2, World Scientific, Singapore, 1995), p1166
30. D. Mukherjee, and S. Pal, Adv. Quant. Chem. **20**, 291 (1989)
31. (a) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quant. Chem. **S13**, 225 (1979) (b) B. R. Brooks, W. D. Laidig, P. Saxe, N. C. Handy, and H. F. Schaefer III, Phys. Scripta **21**, p321 (1980)
32. H. J. Monkhorst, Int. J. Quant. Chem. **S11**, 421 (1977)
33. (a) P. Jorgensen and J. Simons, *Second Quantization based methods in Quantum Chemistry*, (Academic, New York, 1981), p103 (b) ibid, J. Chem. Phys. **79**, 334 (1983)
34. *Geometrical Derivatives of Energy Surface and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht,1986)

35. J. Gauss, in *Modern Methods and Algorithms of Quantum Chemistry*, Proceedings, Second Edition, Edited by J. Grotendorst, (Neumann Institute of Computing Series, Volume 3, Julich, 2000)
36. (a) P. Pulay, in *Applications of Electronic Structure Theory*, Edited by H. F. Schaefer III, (Plenum, New York, 1977), p153 (b) ibid, Adv. Chem. Phys. **69**, 241, (1987)
37. S. T. Epstein, *The Variation Principle in Quantum Chemistry*, (Academic, New York, 1974)
38. N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984)
39. L. Adamowicz, W. D. Laidig, and R. J. Bartlett, Int. J. Quant. Chem. **S18**, 245 (1984)
40. R. J. Bartlett, in *Geometrical Derivatives of Energy Surface and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht,1986), p35
41. T. Helgaker and P. Jorgensen, Adv. Quant. Chem. **19**, 183 (1988)
42. (a) G. Fitzgerald, R. J. Harrison, and R. J. Bartlett, J. Chem. Phys. **85**, 5143 (1986) (b) E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989)
43. P. Jorgensen and T. Helgaker J. Chem. Phys. **89**, 1560 (1988)
44. H. Koch, H. J. A. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria, H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990)
45. J. Olsen, P. Jorgensen, in *Modern Electronic Structure Theory*, Part II, Edited by D. R. Yarkony, (Advanced Series in Physical Chemistry, Volume 2, World Scientific, Singapore, 1995), p857
46. (a) S. Pal, Phys. Rev. **A39**, 39 (1989) (b) S. Pal, Int. J. Quant. Chem. **41**, 443 (1992)
47. (a) D. Ajitha, N. Vaval, and S. Pal, J. Chem. Phys. **110**, 2316 (1999) (b) D. Ajitha and S. Pal, Chem. Phys. Lett. **309**, 457 (1999) (c) D. Ajitha and S. Pal , J. Chem. Phys. **114**, 3380 (2001) (d) N. Vaval and S. Pal, Chem. Phys. Lett. **300**, 125 (1999)

48. D. Ajitha, and S. Pal, Phys. Rev. **A56**, 2658 (1997)
49. P. Szalay, Int. J. Quant. Chem. **55**, 151 (1994)
50. P. Celani, and H. J. Werner, J. Chem. Phys. **119**, 5044 (2003)
51. T. J. Dudley, Y. G. Khait, and M. R. Hoffmann, J. Chem. Phys. **119**, 651 (2003)
52. (a) H. Nakano, K. Hirao, M. S. Gordon, J. Chem. Phys. **108**, 5660 (1998) (b) H. Nakano, N. Otsuka, and K. Hirao in *Recent Advances in Multireference Methods*, Edited by K. Hirao (World Scientific, Singapore, 1999), p131 (b) M. V. Pak and M. S. Gordon, J. Chem. Phys. **118**, 40 (2003)
53. (a) J. F. Stanton, J. Chem. Phys. **99**, 8840 (1993) (b) J. F. Stanton and J. Gauss, J. Chem. Phys. **100**, 4695 (1994) (c) J. F. Stanton and J. Gauss, Theor. Chim. Acta **91**, 267 (1995) (d) S. R. Gwaltney and R. J. Bartlett, J. Chem. Phys. **110**, 62 (1999)
54. S. R. Gwaltney, R. J. Bartlett, and M. Nooijen, J. Chem. Phys. **111**, 58 (1999)
55. D. Ajitha and S. Pal, J. Chem. Phys. **111**, 3832 (1999); **111**, 9892(E) (1999)
56. (a) M. Born, and J. R. Oppenheimer, Ann. Physik. **84**, 457 (1927) (b) M. Born, and K. Huang, in Dynamical Theory of Crystal Lattices, Appendix 8, (Oxford University Press, 1954)
57. B. T. Sutcliffe, *Methods in Computational Molecular Physics*, Edited by S. Wilson and G. H. F. Dierksen, (NATO ASI Series B: Physics, Volume 293, Plenum, New York, 1992), p19
58. (a) D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 111 426 (1928) (b) J. C. Slater, Phys. Rev. **35**, 210 (1930) (c) V. Fock, Z. Physik. **61**, 126 (1930).
59. (a) C. C. J. Roothan, Rev. Mod. Phys. **23**, 69 (1951) (b) ibid, **32**, 179 (1960)
60. J. A. Pople, and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954)

61. (a) J. Paldus, J. Chem. Phys. **61**, 5321 (1974) (b) J. Paldus, in *Theoretical Chemistry: Advances and Perspectives*, Vol. 2, Edited by H. Eyring and D. Henderson (Academic, New York, 1976)
62. F. A. Matsen, and R. Pauncz, *The Unitary Group in Quantum Chemistry*, (Elsevier, Amsterdam, 1986)
63. (a) I. Shavitt, Int. J. Quant. Chem. **S11**, 131 (1977) (b) ibid, **S12**, 5 (1978)
64. (a) J. Karwowski, Theor. Chim. Acta. (Berlin) **29**, 151 (1973) (b) ibid, Chem. Phys. Lett. **19**, 279, (1973)
65. W. Duch and J. Karwowski, Comp. Phys. Reports **2**, 94 (1985)
66. E. R. Davidson, Comp. Phys. **17**, 87 (1975)
67. (a) B. O. Roos, Chem. Phys. Lett. **15**, 153 (1972) (b) B. O. Roos, and P. E. M. Siegbahn, in *Methods of Electronic Structure Theory*, Edited by H. F. Schaefer III, (Plenum, New York, 1977), p277
68. P. E. M. Siegbahn, J. Chem. Phys. **72**, 1647 (1980)
69. A. C. Wahl and G. Das, in *Methods of Electronic Structure Theory*, Edited by H. F. Schaefer III, (Plenum, New York, 1977), p51
70. (a) B. O. Roos, Adv. Chem. Phys. **69**, 399 (1987) (b) H.-J. Werner, Adv. Chem. Phys. **69**, 1 (1987) (c) R. Shepard, Adv. Chem. Phys. **69**, 63 (1987)
71. W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Acc. Chem. Res. **6**, 368 (1973)
72. P. R. Taylor, *Lecture Notes in Quantum Chemistry: European Summer School*, (Springer-Verlag, Berlin, 1994), p125
73. J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quant. Chem. **S10**, 1 (1977)

74. R. Chaudhary, D. Mukherjee, and M. D. Prasad, in *Aspects of Many-Body Effects in Molecules and Extended Systems*, Edited by D. Mukherjee, Lecture Notes in Chemistry, Vol. 50, (Springer-Verlag, Heidelberg, 1989), p3
75. H. Primas, in *Modern Quantum Chemistry*, Edited by O. Sinanoglu, Vol. 2, (Academic, New York, 1965), p45
76. K. A. Bruckner, Phys. Rev. **97**, 1353 (1955) (b) ibid, Phys. Rev. **100**, 36 (1955)
77. A. L. Fetter, and J. D. Walecka, *Quantum Theory of Many-Particle Systems*, (McGraw-Hill, New York, 1971)
78. J. Linderberg, and Y. Ohrn, Propagators in Quantum Chemistry, (Academic, London, 1973)
79. (a) D. J. Rowe, Rev. Mod. Phys. **40**, 153 (1968) (b) T. I. Shibuya and V. McKoy, Phys. Rev. **A2**, 2208 (1970)
80. (a) H. P. Kelly, Phys. Rev. **131**, 684 (1963) (b) ibid, **144**, 39, (1966) (c) ibid, Adv. Chem. Phys. **14**, 129 (1969)
81. K. F. Freed, Annu. Rev. Phys. Chem. **21**, 313 (1972)
82. L. Z. Stolarczyk, and H. J. Monkhorst, Phys. Rev. **A32**, 725 (1986)
83. W. Kutzelnigg, in *Aspects of Many-Body Effects in Molecules and Extended Systems*, Edited by D. Mukherjee, Lecture Notes in Chemistry, Vol. 50, (Springer-Verlag, Heidelberg, 1989), p35
84. (a) J. Goldstone, Proc. Roy. Soc. **A239**, 267 (1957) (b) N. M. Hugenholtz, Physica **23**, 481 (1957) (c) J. Hubbard, Proc. Roy. Soc. **A240**, 539 (1957)
85. (a) F. Coester, Nucl. Phys. **7**, 421 (1958) (b) F. Coester, H. Kummel, Nucl. Phys. **17**, 477 (1960)
86. R. K. Nesbet, Adv. Chem. Phys. **9**, 321 (1968)

87. (a) W. Meyer, Int. J. Quant. Chem. **5**, 341, (1971) (b) ibid, J. Chem. Phys. **58**, 10175 (1973)
88. (a) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quant. Chem. **14**, 546 (1978) (b) R. J. Bartlett, and G. D. Purvis III, Int. J. Quant. Chem. **14**, 561 (1978)
89. J. Paldus, J. Cizek, and I. Shavitt, Phys. Rev. **A52**, 5 (1972)
90. G. D. Purvis III, R. J. Bartlett, J. Chem. Phys. **96**, 7041 (1982)
91. J. Noga, and R. J. Bartlett, J. Chem. Phys. **96**, 7041 (1987)
92. S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **97**, 4282 (1992)
93. (a) K. F. Freed, Phys. Rev. **173**, 1 (1968) (b) M. A. Robb, in *Computational techniques in Quantum Chemisty and Molecular Physics*, Edited by G. H. F. Diercksen, B. T. Sutcliffe, and A. Veillard, (NATO ASI Series C: Mathematical and Physical Sciences, Vol. 15, Riedel, Dordrecht, 1975), p435
94. W. Kutzelnigg, in *Methods of electronic structure theory*, Edited by H. F. Schaefer III, (Plenum Press, New York, 1977), p129
95. R. J. Gdanitz, and R. Ahlrichs, Chem. Phys. Lett. **143**, 413 (1988)
96. (a) P. G. Szalay and R. J. Bartlett, Chem. Phys. Lett. **214**, 481 (1993) (b) ibid, J. Chem. Phys. **103**, 3600 (1995)
97. J. P. Daudey, J. L. Heully, and J. P. Malrieu, J. Chem. Phys. **99**, 1240 (1993)
98. See, e.g. M. Urban, P. Neogrady, and I. Hubac, in *Recent Advances in Coupled-Cluster Methods*, Edited by R. J. Bartlett, (World Scientific, Singapore, 1997), p275 and references therein.

99. (a) C. L. Janssen, and H. F. Schaefer III, Theor. Chim. Acta. **79**, 1 (1991) (b) X. Li and J. Paldus, J. Chem. Phys. **101**, 8812 (1994) (c) M. Nooijen, and R. J. Bartlett, J. Chem. Phys. **104**, 2652 (1996)

100. X. Li, and J. Paldus, in *Recent Advances in Coupled-Cluster Methods*, Edited by Bartlett, (World Scientific, Singapore, 1997), p183

101. (a) H. Nakatsuji, Chem. Phys. Lett. **59**, 362 (1978) (b) H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978) (c) ibid, **68**, 4279 (1978) (d) K. Hirao, J. Chem. Phys. **95**, 3589 (1991)

102. (a) M. Rittby and R. J. Bartlett, J. Phys. Chem. **92**, 3033 (1988) (b) J. D. Watts and R. J. Bartlett, J. Chem. Phys. **97**, 4282 (1992) (c) P. G. Szalay and J. Gauss, J. Chem. Phys., **107**, 9028 (1997)

103. (a) D. Jayatilaka, and T. J. Lee, Chem. Phys. Lett. **199**, 211 (1992) (b) ibid, J. Chem. Phys. **98**, 9734, (1993) (c) T. J. Lee and D. Jayatilaka, Chem. Phys. Lett. **201**, 1 (1993)

104. P. J. Knowles, C. Hampel, and H. J. Werner, J. Chem. Phys. **99**, 5219 (1993)

105. (a) S. Pal, M. D. Prasad, and D. Mukherjee, Pramana, **18**, 261 (1982) (b) S. Pal, M. D. Prasad, and D. Mukherjee, Theor. Chim. Acta. **62**, 523 (1983) (c) ibid. **66**, 311 (1984) (d) S. Pal, Theor. Chim. Acta. **66**, 151 (1984)

106. (a) S. Pal, and K. B. Ghose, Cur. Sci. **63**, 667 (1992) (a) K. B. Ghose, P. G. Nair, and S. Pal, Chem. Phys. Lett. **211**, 15 (1993) (b) N. Vaval, K. B. Ghose, P. G. Nair, and S. Pal, Proc. Ind. Acad. Sci. **106**, 387 (1994)

107. (a) R. J. Bartlett, and J. Noga, Chem. Phys. Lett. **150**, 29 (1988) (b) R. J. Bartlett, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **155**, 133 (1989) (c) R. J. Bartlett, S. A. Kucharski, J. Noga, J. D. Watts, and G. W. Trucks in *Aspects of many-body effects in*

molecules and extended systems, Lecture notes in Chemistry, edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p125 (d) P. G. Szalay, M. Nooijen, and R. J. Bartlett, J. Chem. Phys. **103**, 281 (1995) (e) P. Piecuch, and R. J. Bartlett, Adv. Quant. Chem. **34**, 295 (1999)

108. (a) J. Arponen, Ann. Phys. (N.Y.) **151**, 311 (1983) (b) J. Arponen, R. F. Bishop, and E. Pajanne, Phys. Rev. **A36**, 2519 (1987) (c) ibid, **A36**, 2539 (1987) (d) R. F. Bishop, J. Arponen, and E. Pajanne, in *Aspects of many-body effects in molecules and extended systems, Lecture notes in Chemistry,* edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p78
109. (a) S. Pal, Theor. Chim. Acta **62**, 523 (1983) (b) ibid, Phys. Rev. **A33**, 2240 (1986) (c) N. Vaval, K. B. Ghose, and S. Pal, J. Chem. Phys. **101**, 4914 (1994) (d) N. Vaval, and S. Pal, Phys. Rev. **A54**, 250 (1996) (e) A. B. Kumar, N. Vaval, and S. Pal, Chem. Phys. Lett. **295**, 189 (1998) (f) N. Vaval, A. B. Kumar, and S. Pal, Int. J. Mol. Sci. **2**, 89 (2001) (g) N. Vaval, Chem. Phys. Lett. **318**, 168 (2000) (h) P. U. Manohar, N. Vaval, and S. Pal, Chem. Phys. Lett. **387**, 442 (2004)
110. R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974)
111. P. E. M. Siegbahn, Int. J. Quant. Chem. **18**, 1229 (1980)
112. J. Lischka, R. Shepard, F. B. Brown, and I. Shavitt, Int. J. Quant. Chem. **S15**, 91 (1981)
113. V. R. Saunders, and J. H. van Lenthe, Mol. Phys. **48**, 923 (1983)
114. W. Meyer, in *Methods of Electronic Structure Theory*, Edited by H. F. Schaefer III, (Plenum, New York, 1977), p413

115. (a) H. J. Werner, and E. A. Reinsch, J. Chem. Phys. **76**, 3144 (1982) (b) H. J. Werner, and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988) (c) P. J. Knowles, and H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988)

116. J. P. Malrieu, J. P. Daudey, and R. Caballol, J. Chem. Phys. **101**, 8908 (1994)

117. P. G. Szalay in *Recent Advances in Coupled-Cluster Methods*, Edited by R. J. Bartlett, (World Scientific, Singapore, 1997), p81

118. L. Adamowicz, and J. P. Malrieu, in *Recent Advances in Coupled-Cluster Methods*, Edited by R. J. Bartlett, (World Scientific, Singapore, 1997), 307

119. I. Shavitt, Int. J. Mol. Sci. **3**, 639, (2002)

120. (a) B. O. Roos, P. Linse, P. E. M. Siegbahn, and M. R. A. Blomberg, Chem. Phys. **66**, 197 (1982) (b) K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej, K. Wolinski, J. Phys. Chem. **94**, 5483 (1990) (c) K. Andersson, P. A. Malmqvist, B. O. Roos, J. Chem. Phys. 96, 1218 (1992) (d) K. Andersson, Theor. Chim. Acta, **91**, 31 (1995) (e) K. Andersson, and B. O. Roos, B. O. Chem. Phys. Lett. **191**, 507 (1992) (f) ibid, Int. J. Quant. Chem. **45**, 591 (1993) (g) K. Andersson, B. O. Roos, P. A. Malmqvist, and P. O. Widmark, Chem. Phys. Lett. **230**, 391 (1994)

121. (a) K. Wolinski, H. L. Sellers, and P. Pulay, Chem. Phys. Lett. **140**, 225 (1987) (b) K. Wolinski, and P. Pulay, J. Chem. Phys, **90**, 3647 (1989) (c) K. Wolinski, Theor. Chim. Acta, **82**, 459 (1992)

122. K. G. Dyall, J. Chem. Phys. **102**, 4909 (1995)

123. P. Celani, and H. J. Werner, J. Chem. Phys. **112**, 5546 (2000)

124. (a) R. B. Murphy and R. P. Messmer, Chem. Phys. Lett. **183**, 443 (1991) (b) R. B. Murphy and R. P. Messmer, J. Chem. Phys. **97**, 4170 (1992)

125. (a) K. Hirao, Chem. Phys. Lett. **190**, 374 (1992) (b) K. Hirao, Chem. Phys. Lett. **196**, 397 (1992) (c) K. Hirao, Chem. Phys. Lett. **201**, 59 (1993)

126. (a) P. M. Kozlowski and E. R. Davidson, Chem. Phys. Lett. **222**, 615 (1994) (b) P. M. Kozlowski and E. R. Davidson, Chem. Phys. Lett. **226**, 440 (1994) (c) P. M. Kozlowski and E. R. Davidson, J. Chem. Phys. **100**, 3672 (1994)

127. H. J. van Dam, J. H. van Lenthe, and P. Pulay, Mol. Phys. **93**, 431 (1998)

128. C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, and J.-P. Malrieu, J. Chem. Phys. **114**, 10252 (2001)

129. (a) H. Nakano, and K. Hirao, Chem. Phys. Lett. **317**, 90 (2000) (b) H. Nakano, J. Nakatani, and K. Hirao, J. Chem. Phys. **114**, 1133 (2001) (c) H. Nakano, and K. Hirao, Bull. Korean Chem. Soc. **24**, 812 (2003)

130. H. J. Werner, Mol. Phys. **89**, 645 (1996)

131. P. Durand, and J. P. Malrieu, Adv. Chem. Phys. **67**, 321 (1987)

132. V. Hurtubise, and K. F. Freed, Adv. Chem. Phys. **83**, 465 (1993)

133. L. Meissner, and M. Nooijen, J. Chem. Phys. **102**, 9604 (1995)

134. I. Lindgren, and D. Mukherjee, Phys. Rep. **151**, 93 (1987)

135. (a) T. Kato, Prog. Theor. Phys. **4**, 514 (1949) (b) C. Bloch, Nucl. Phys. **6**, 329 (1958) (c) J. des Cloizeaux, Nucl. Phys. **20**, 321 (1960) (d) ibid, Phys. Rev. **135**, 685 (1964) (e) ibid, Phys. Rev. **135**, 698 (1964)

136. (a) F. Jorgensen, and T. Pedersen, Mol. Phys. **27**, 33 (1974) (b) ibid, **27**, 959 (1974) (c) ibid, **28**, 599 (1974) (d) F. Jorgensen, T. Pedersen, and A. Chedin, Mol. Phys. **30**, 1377 (1975) (e) F. Jorgensen, Mol. Phys. **29**, 1137 (1975) (f) ibid, Int. J. Quant. Chem. **12**, 397 (1977)

137. (a) H. Feschbach, Ann. Phys. (N.Y.) **5**, 357 (1958) (b) ibid, **19**, 287 (1962) (c) P. O. Lowdin, J. Math. Phys. **3**, 969 (1962)

138. B. Kirtman, J. Chem. Phys. **75**, 798 (1981)

139. (a) J. P. Malrieu, P. Durand, and J. P. Daudey, J. Phys. **A18**, 809 (1985) (b) J. L. Heully, and J. P. Daudey, J. Chem. Phys. **88**, 1046 (1987) (c) A. V. Zaitsevskii, and J. L. Heully, J. Phys. **B25**, 603 (1992)

140. (a) D. Mukhopadhyay, B. Datta, and D. Mukherjee, Chem. Phys. Lett. **197**, 236 (1992) (b) B. Datta, R. Chaudhury, and D. Mukherjee, J. Mol. Struct.: THEOCHEM, **361**, 21 (1996)

141. (a) L. Meissner, Chem. Phys. Lett. **255**, 244 (1996) (b) L. Meissner, P. Malinowski, Phys. Rev. **A61**, 062510 (2000) (c) P. Malinowski, L. Meissner, and A. Nowaczyk, J. Chem. Phys. **116**, 7362 (2002) (d) L. Meissner, and J. Gryniakow, Coll. Check. Chem. Comm. **68**, 105 (2003)

142. (a) B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967) (b) ibid, Adv. Quant. Chem. **10**, 187 (1977)

143. (a) I. Lindgren, J. Phys. **B7**, 2441 (1974) (b) ibid, Int. J. Quant. Chem. **S12**, 33 (1978)

144. D. J. Klein, J. Chem. Phys. **61**, 786 (1974)

145. (a) V. Kvasanicka, Czech. J. Phys. **B24**, 605 (1974) (b) ibid, Adv. Chem. Phys. **36**, 345 (1977)

146. (a) M. G. Sheppard, and K. F. Freed, J. Chem. Phys. **75**, 4507 (1981) (b) ibid, **75**, 4525 (1981) (c) K. F. Freed, Acc. Chem. Res. **16**, 137 (1983) (d) K. F. Freed, in *Many-Body Methods in Quantum Chemistry*, Edited by U. Kaldor, (Springer, Berlin, 1989), p1 (e) M. G. Sheppard, K. F. Freed, M. F. Herman, and D. L. Yeager, Chem.

Phys. Lett. **61**, 577 (1979) (f) S. Iwata, and K. F. Freed, J. Chem. Phys. **65**, 1071 (1976) (g) ibid, **66**, 1765, (1977)

147. (a) P. Westhaus, Int. J. Quant. Chem. **S7**, 463 (1973) (b) P. Westhaus, E. G. Bradford, and D. Hall, J. Chem. Phys. **62**, 1607 (1977)
148. (a) K. Suzuki, Prog. Theor. Phys. **58**, 1064 (1977) (b) L. T. Redmon, and R. J. Bartlett, J. Chem. Phys. **76**, 1938 (1982)
149. I. Shavitt, and L. T. Redmon, J. Chem. Phys. **73**, 5711 (1980)
150. (a) B. Kirtman, J. Chem. Phys. **49**, 3890 (1968) (b) ibid, **75**, 798 (1981) (c) P. R. Certain, and J. O. Hirschfelder, J. Chem. Phys. **52**, 5977 (1970) (d) ibid, **53**, 2992 (1970)
151. M. A. Haque, and D. Mukherjee, Pramana, **23**, 651 (1984)
152. (a) T. H. Schucan and H. A. Weidenmuller, Ann. Phys. (N.Y.) **73**, 108 (1972) (b) ibid. **76**, 483 (1973)
153. G. Hose and U. Kaldor, J. Phys. **B12**, 3827 (1979)
154. B. H. Brandow, in *New Horizons in Quantum Chemistry*, edited by P. O. Lowdin and B. Pullman, (Riedel, Dordrecht, 1983)
155. (a) I. Lindgren, Phys. Scripta **32**, 291 (1985) (b) ibid, **32**, 611 (1985)
156. (a) D. Mukherjee, Proc. Ind. Acad. Sci. **96**, 145 (1986) (b) D. Mukherjee, Chem. Phys. Lett. **125**, 207 (1986) (c) D. Mukherjee, Int. J. Quant. Chem. **S20**, 409 (1986)
157. R. Chowduri, D. Mukhopadhyay, and D. Mukherjee, in in *Aspects of Many-Body Effects in Molecules and Extended Systems*, Edited by D. Mukherjee, Lecture Notes in Chemistry, Vol. 50, (Springer-Verlag, Heidelberg, 1989), p165
158. L. Meissner, and R. J. Bartlett, J. Chem. Phys. **91**, 4800 (1989)

159. (a) P. S. Stern, and U. Kaldor, J. Chem. Phys. **63**, 2199 (1976) (b) ibid, **64**, 2002 (1976)

160. (a) H. Nakano, J. Chem. Phys. **99**, 7983 (1993) (b) ibid, Chem. Phys. Lett. **207**, 372 (1993)

161. (a) G. Hose, and U. Kaldor, Phys. Scripta. **21**, 357 (1980) (b) ibid. Chem. Phys. **62**, 419 (1981) (c) ibid. J. Phys. Chem. **86**, 2133 (1982)

162. B. Jezioroski and H. J. Monkhorst, Phys. Rev. **A24**, 1968 (1982)

163. (a) D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. **33**, 955 (1977) (b) D. Mukherjee, Pramana **12**, 203 (1979) (c) D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Ind. J. Pure and Applied Phys. **15**, 613 (1977) (d) A. Mukhopadhyay, R. K. Moitra, and D. Mukherjee, J. Phys. **12**, 1 (1977) (e) M. A. Haque and D. Mukherjee, J. Chem. Phys. **80**, 5058 (1984) (d)

164. (a) R. Offermann, W. Ey, and H. Kummel, Nucl. Phys. **A273**, 349 (1976) (b) R. Offermann, Nucl. Phys. **A273**, 368 (1976) (c) W. Ey, Nucl. Phys. **A296**, 189 (1978)

165. (a) H. Reitz, and W. Kutzelnigg, Chem. Phys. Lett. **66**, 11 (1979) (b) W. Kutzelnigg, J. Chem. Phys. **77**, 3081 (1981) (c) ibid, **80**, 822 (1984) (d) W. Kutzelnigg and S. Koch, J. Chem. Phys. **79**, 4315 (1983)

166. L. Z. Stolarczyk and H. J. Monkhorst, Phys. Rev. **A32**, 725 (1986) (b) ibid, **A32**, 743 (1986)

167. B. Jezioroski, and J. Paldus, J. Chem. Phys. **90**, 2714 (1989)

168. (a) W. Kutzelnigg, D. Mukherjee, and H. Koch, J. Chem. Phys. **87**, 5902 (1987) (b) D. Mukherjee, W. Kutzelnigg, and H. Koch, J. Chem. Phys. **87**, 5911 (1987) (c) S. Koch and D. Mukherjee, Chem. Phys. Lett. **145**, 321 (1988)

169. (a) M. A. Haque, and U. Kaldor, Chem. Phys. Lett. **117**, 347 (1985) (b) ibid, **120**, 261 (1985)

170. (a) R. Mattie, M. Rittby, R. J. Bartlett, and S. Pal, in *Aspects of many-body effects in molecules and extended systems, Lecture notes in Chemistry,* edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p143 (b) U. Kaldor, in same volume, p154

171. S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, J. Chem. Phys. **88**, 4357 (1988)

172. (a) S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, Chem. Phys. Lett. **137**, 273 (1987) (b) N. Vaval, S. Pal, and D. Mukherjee, Theor. Chem. Acc. **99**, 100 (1998) (c) N. Vaval, and S. Pal, J. Chem. Phys. **111**, 4051 (1999)

173. S. R. Hughes, and U. Kaldor, Phys. Rev. **A47**, 4705 (1993)

174. L. Meissner, J. Chem. Phys. **103**, 8014 (1995)

175. M. Nooijen, J. Chem. Phys. **104**, 2638 (1996)

176. (a) H. J. Monkhorst, Int. J. Quantum Chem. **S11**, 421 (1977) (b) E. Dalgaard, and H. J. Monkhorst, Phys. Rev. **A28**, 1217 (1983)

177. (a) D. Mukherjee and P. K. Mukherjee, Chem. Phys. **37**, 325 (1979) (b) S. Ghosh, D. Mukherjee, and S. N. Bhattacharya, Mol. Phys. **43**, 173 (1981) (c) S. Ghosh and D. Mukherjee, Proc. Ind. Acad. Sci. **93**, 947 (1984)

179. (a) H. Koch, and P. Jorgensen, J. Chem. Phys. **93**, 3333 (1990) (b) H. Koch, H. J. A. Jensen, P. Jorgensen, and T. Helgaker, J. Chem. Phys. **93**, 3345 (1990)

180. (a) H. Sekino, and R. J. Bartlett, Int. J. Quantum Chem. **S18**, 255 (1984) (b) J. Geertsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989) (c) J. F. Stanton, and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993) (d) D. C. Comeau, and R. J. Bartlett, Chem. Phys. Lett. **207**, 414 (1993) (e) J. F. Stanton, and J. Gauss, J. Chem.

Phys. **101**, 8938 (1994) (f) M. Nooijen, and R. J. Bartlett, J. Chem. Phys, **102**, 3629 (1995) (g) S. R. Gawlitsky, M. Nooijen, and R. J. Bartlett, Chem. Phys. Lett. **248**, 189 (1996)

181. (a) M. Nooijen, and R. J. Bartlett, J. Chem. Phys. **106**, 6441 (1997) (b) ibid, **106**, 6449 (1997) (c) ibid, **107**, 6812 (1997)

182. (a) H. Nakatsuji, Chem. Phys. Lett. **59**, 362 (1978) (b) ibid, **67**, 329 (1979) (c) H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978) (d) ibid, **68**, 4279 (1978)

183. (a) L. Meissner, and R. J. Bartlett, J. Chem. Phys. **94**, 6670 (1991) (b) L. Meissner and R. J. Bartlett, J. Chem. Phys. **92**, 561 (1990)

184. D. Sinha, S. Mukhopadhyay, and D. Mukherjee, Chem. Phys. Lett. **129**, 369 (1986)

185. J. E. Rice and R. D. Amos, Chem. Phys. Lett. **122**, 585 (1985)

186. G. Fitzgerald, R. J. Harrison, R.J. Bartlett, Chem. Phys. Lett. **117**, 433 (1985)

187. A. C. Scheiner, G. E. Scuseria, T. J. Lee, and H. F. Schaefer III, J. Chem. Phys. **87**, 5361 (1987)

188. E. A. Salter and R. J. Bartlett, J. Chem. Phys. **90**, 1767 (1989)

Chapter II

Formulation of analytic response approach and Z-vector method for state-universal multi-reference coupled cluster theory.

II.1 Introduction

Among the theories developed to describe electron correlation effects in quasi-degenerate situations, effective Hamiltonian based MRCC methods have been well-understood and established.[1-3] As discussed in first chapter, there are two main MRCC variants which are applicable in different situations. The first one, the valence-universal variant (VUMRCC) or the Fock-space variant (FSMRCC), is suitable for computation of spectroscopic quantities based on energy differences between states with same or different number of electrons, such as ionization potential, electron affinity and excitation energies.[4] The second one, the state-universal variant (SUMRCC) or the Hilbert-space variant (HSMRCC), is suitable for description of potential energy surfaces.[5-6] Several applications of both these theories have been reported.[1-6]

As mentioned in first chapter, the standard SRCC theory was originally cast in a non-variational (or non-stationary) framework. Due to this, the expression for a first-order property in SRCC depended explicitly on first-derivatives of cluster amplitudes with respect to the external perturbation, and it seemed to be necessary to compute these cluster amplitude derivatives for all modes of perturbation. This impediment was overcome by Bartlett and coworkers[7] for first-order molecular properties by using the idea of the algebraic Z-vector method introduced by Handy and Schaefer[8] in their analysis of analytic derivatives for CI method. This development significantly contributed to efficient implementation of SRCC gradients. Later on, using constrained variation approach, Koch, Helgaker, Jorgensen and coworkers[9] recast the SRCC theory into a variational (or stationary) framework by incorporating a set of de-excitation amplitudes which were shown to be same as the Z-vector.

Later in the thesis, we develop a variational formulation of effective Hamiltonian based MRCC theories which is appropriate for computation of molecular properties. However, in this chapter, we first introduce the algebraic elimination method to generalize the Z-vector method for effective Hamiltonian based MRCC theories by using SUMRCC theory as an example. Using the time-independent form of the response approach followed by Monkhorst[10] in SRCC and Pal[11] in MRCC, a framework for analytic computation of molecular response properties in SUMRCC is obtained. The structure of resulting equations for first-order properties is analyzed to facilitate generalization of Z-vector method. Two different ways to carry out Handy-Schaefer type of elimination are identified and studied in detail.

II.2 Brief description of state-universal MRCC theory

The state-universal MRCC theory was proposed by Jezioroski and Monkhorst[12] (J&M) as an alternative to other MRCC theories using valence-universal or Fock-space strategy. The resulting cluster expansion for the wave function is a generalization of the one introduced by Silverstone and Sinanoglu.[13] Unlike VUMRCC theories where the Schrödinger equation is considered within the Fock-space with different number of valence electrons, the main idea in SUMRCC is to find an MRCC ansatz with well defined cluster amplitudes by staying within the Hilbert-space of a fixed number of electrons N relevant to the problem. The redundancy problem of cluster amplitudes is eliminated by postulating that the wave-operator is state-universal, i.e., it is the same for a subset of exact N-electron states under consideration. This naturally leads to effective Hamiltonian approach.

As discussed in first chapter, a quasi-degenerate system is characterized by the existence of a set of strongly interacting determinants $\left\{\Phi_\mu, \forall\mu = 1, M\right\}$ spanning the model space P. The choice of determinants to be included in P is usually made by using orbital energies as a guide. This leads both complete and incomplete model spaces. In this chapter, we assume that P is a complete model space. Incomplete model spaces will be considered in fifth chapter. As described in first chapter, in SUMRCC theory, a cluster operator T_μ is associated with each model space determinant Φ_μ acting as vacuum. In terms of T_μ and projector P_μ, wave-operator is written as follows.

$$\Omega = \sum_\mu e^{T_\mu} P_\mu \tag{2.1}$$

The cluster operator T_μ is very similar in structure to the SRCC cluster operator T. It is expanded in terms of commuting set of excitation operators defined with respect to vacuum Φ_μ.

$$T_\mu = T_{\mu 1} + T_{\mu 2} + \cdots + T_{\mu N} \tag{2.2}$$

$$T_{\mu I} = \frac{1}{(I!)^2} \sum_{\substack{ijk\ldots \\ abc..}} t_{abc\ldots}^{rst\ldots} a_r^\dagger a_s^\dagger a_t^\dagger \ldots a_c a_b a_a \tag{2.3}$$

Here, summation labels $a, b, c, \ldots (r, s, t, \ldots)$ refer to the orbitals occupied (unoccupied) in Φ_μ, and the operators $a_a, a_b, a_c, \ldots (a_r^\dagger, a_s^\dagger, a_t^\dagger, \ldots)$ are the corresponding second-quantized orbital annihilation (creation) operators. To enforce intermediate normalization $P\Omega P = P$ for the wave-operator, valence-only excitations are excluded in the cluster amplitudes T_μ by setting corresponding cluster amplitudes to zero. Just as in

SRCC where e^T acting on the vacuum Φ generates corresponding correlated wavefunction Ψ, similarly, in SUMRCC, the action of e^{T_μ} on corresponding vacuum Φ_μ, generates a partly correlated wavefunction Ψ_μ. The final wave-functions for different states under consideration are written as different linear combinations of these partly correlated wave-functions.

$$\Psi_I = \sum_\mu c_\mu^I \Psi_\mu \tag{2.4}$$

Here, the label I denotes a particular state among the quasi-degenerate states under consideration and quantities c_μ^I are referred to as model space coefficients for that state. To determine cluster amplitudes, Eq (2.1) defining the wave-operator is substituted into generalized Bloch equation $\hat{H}\Omega P = \Omega P H_{eff} P$ discussed in first chapter. This leads to,

$$\hat{H}e^{T_\mu}\left|\Phi_\mu\right\rangle = \sum_\nu e^{T_\nu} H_{eff}^{\nu\mu} \qquad \forall\mu \tag{2.5}$$

There are two approaches for solving this equation. The first approach, followed by J&M, is similar to the pre-multiplication method used in deriving SRCC equations. Pre-multiplication of Eq (2.5) by e^{-T_μ} followed by left projection with Q and P leads to the following equations.

$$\left\langle\Phi_\mu^*\right|e^{-T_\mu}\hat{H}e^{T_\mu}\left|\Phi_\mu\right\rangle = \sum_{\nu\neq\mu}\left\langle\Phi_\mu^*\right|e^{-T_\mu}e^{T_\nu}\left|\Phi_\nu\right\rangle H_{eff}^{\nu\mu} \qquad \forall\mu \tag{2.6}$$

$$H_{eff}^{\nu\mu} = \left\langle\Phi_\nu\right|e^{-T_\mu}\hat{H}e^{T_\mu}\left|\Phi_\mu\right\rangle \qquad \forall\mu,\nu \tag{2.7}$$

$$H_{eff}C = CE \tag{2.8}$$

$$\tilde{C}H_{eff} = E\tilde{C} \tag{2.9}$$

$$\tilde{C}H_{eff}C = E \tag{2.10}$$

$$\tilde{C}C = C\tilde{C} = I \tag{2.11}$$

Here, $\{\Phi_{\mu}^{*}\}$ denotes the set of determinants in Q organized as a hole-particle excitation out of Φ_{μ}. While, Eq (2.6) is the determining equation for cluster amplitudes T_{μ}, Eq (2.7) defines an non-hermitian $M \times M$ dimensional Bloch effective Hamiltonian matrix $H_{eff}^{\nu\mu}$. Eqs (2.8)-(2.9) are defining equations for the diagonalisation of $H_{eff}^{\nu\mu}$, and yield the right and left side model space coefficient matrices, C and $\tilde{C}$ respectively. While Eq (2.10) defines a diagonal matrix E containing energy of M quasi-degenerate states under consideration, Eq (2.11) defines a biorthonormalization relation between C and $\tilde{C}$.

As noted by J&M, the cluster amplitude Eq (2.7) exhibits a structure very similar to the SRCC equations. Its left hand side is same as SRCC cluster amplitude equations and referred to as the direct term. As in SRCC, it is explicitly connected due to Baker-Campbell-Hausdorf (BCH) formula for $e^{-T_{\mu}}He^{T_{\mu}}$. The terms on right hand side couple the cluster amplitudes of different vacuums and are referred to as renormalization terms. Using the BCH formula for $e^{-T_{\mu}}e^{T_{\nu}}$, J&M sketch a special perturbative proof of connectivity of cluster amplitudes and effective Hamiltonian. The renormalization terms generate all folded diagrams of Brandow's open-shell MBPT.[14] As first suggested by Hose and Kaldor[15] and adopted by J&M in their SUMRCC formulation, the quantities $\{H_{eff}^{\nu\mu}, \forall\, \nu = 1,\ldots,M\}$ are evaluated by using normal-ordered expressions for $\hat{H}$ with respect to determinant Φ_{μ} as vacuum.

$$\hat{H} = H_0(\mu) + H_{0N}(\mu) + F_N(\mu) + V_N \tag{2.12}$$

Here, $H_0(\mu)$ is expectation value of $\hat{H}$ with respect to Φ_μ and subscript N denotes normal-ordering. $H_{0N}(\mu)$ is a diagonal one-body operator containing orbital energies, $F_N(\mu)$ is a general one-body operator and V_N is the usual two-body operator containing two-electron repulsion integrals. Detailed expressions for elements of $F_N(\mu)$ depend on how the orbitals are obtained as well as the reference vacuum.[16]

Truncation schemes for cluster operators and renormalization terms for practical computations were discussed by J&M in their original work. Renormalization terms arising due to the use of BCH formula for $e^{-T_\mu}e^{T_\nu}$ are very complicated and result in enormous number of diagrams requiring further truncation. Jezioroski, Paldus, Piecuch and coworkers[6,17] have made a systematic study of different truncations for direct as well as renormalization terms, in context of their orthogonally spin-adapted version of SUMRCC theory with singles and doubles approximation (SUMRCCSD), employing two-dimensional model space containing closed-shell type of configurations. It has been applied to study quasi-degeneracy effects in H_4 and H_8 model systems at different geometries[17]

Although BCH formula leads to size-extensivity even under different truncations, cumbersome nature of resulting renormalization terms has led to a second method of solution of SUMRCC equations avoiding the use of BCH formulas. Followed by Meissner, Kucharski, Balkova, Bartlett and coworkers[7,16,18] this method involves left projection of Eq (2.5) with Q and P leading to the following equations in place of (2.6)-(2.7).

$$\left\langle \Phi_\mu^* \middle| \hat{H} e^{T_\mu} \middle| \Phi_\mu \right\rangle = \sum_\nu \left\langle \Phi_\mu^* \middle| e^{T_\nu} \middle| \Phi_\nu \right\rangle H_{eff}^{\nu\mu} \qquad \forall \mu \tag{2.13}$$

$$H_{eff}^{\nu\mu} = \left\langle \Phi_\nu \middle| \hat{H} e^{T_\mu} \middle| \Phi_\mu \right\rangle \qquad \forall \mu, \nu \tag{2.14}$$

In absence of BCH formulas, the above equations contain unlinked and disconnected terms. As is done in SRCC theory, Kucharski and Bartlett[16] demonstrated the cancellation of unlinked terms in above equations leading to size-extensive quantities. They have also presented the resulting SUMRCC equations in diagrammatic form using singles and doubles approximation for cluster operators T_{μ}, for model spaces with up to six-fold excitations. This method has been applied to study bond-breaking in simple molecules such as Li_2.[19] Berkovic and Kaldor[20] have also presented some applications of SUMRCC theory within singles and doubles approximation.

Use of complete model spaces often suffers from intruder state problems. Although incomplete model spaces were considered by J&M in their original work, for some time it was not possible to achieve size-extensivity for such model spaces. Later on, closely following the work of Mukherjee[1-2] on incomplete model space based Fock-space approaches, Meissner[21-22] obtained size-extensive SUMRCC theory using general incomplete model spaces. Balkova and coworkers[23-25] and Berkovic and Kaldor[26] have carried out some applications of this approach for some special classes of incomplete model spaces.

II.3 Analytic response approach for state-universal MRCC theory

SUMRCC is potentially useful for studying ground and close-lying excited state potential energy surfaces for a wide range of geometries. Study of molecular properties and property surfaces using SUMRCC requires development of an analytic response approach. In this section, we apply time-independent response approach along the lines of Monkhorst[10] and Pal[11] to obtain a framework for analytic computation of first-order energy response properties such as dipole moment or molecular energy gradients. Recently, Szalay[27] has used a constrained variation approach for SUMRCC to carry out a theoretical analysis on the cost of a gradient calculation in SUMRCC relative to a SRCC gradient calculations. Relationship between Szalay's approach and the SUMRCC Z-vector approach followed here will be analyzed in the third chapter.

As discussed in first chapter, expressions for various static properties can be obtained by applying a static external perturbation (also referred to as external field) $\hat{H}^{(1)}$ with strength parameter g. The Hamiltonian in presence of external field becomes dependent on field strength parameter g and is denoted as $\hat{H}(g)=\hat{H}+g\hat{H}^{(1)}$. The perturbation is assumed to be weak enough so that Taylor series expansion for various quantities is possible. In presence of perturbation, all SUMRCC parameters, collectively denoted by $\Theta=\{T_\mu, H_{eff}^{\mu\nu}, C, \tilde{C}, E\}$ become functions of perturbation strength parameter g and can be expanded as follows.

$$\Theta(g)=\Theta^{(0)}+g\Theta^{(1)}+\tfrac{1}{2!}g^2\Theta^{(2)}+\cdots \tag{2.15}$$

In the above equation, bracketed superscript denotes the order of the perturbation. Substituting Eq (2.15) into Eq (2.6)-(2.11) and collecting terms of same order in perturbation leads to hierarchical equations for various response quantities. For zeroth-order terms, we get back Eq (2.6)-(2.11). Henceforth, we drop superscript indicating order for zeroth-order quantities and they are simply denoted by Θ. Collecting terms linear in perturbation, we get expression for first-order energy response for all states within the manifold, written as a diagonal matrix $E^{(1)}$, in terms of other first-order response quantities $T^{(1)}$, $H_{eff}^{(1)}$, $C^{(1)}$ and $\tilde{C}^{(1)}$.

$$E^{(1)}=\tilde{C}H_{eff}^{(1)}C+\tilde{C}^{(1)}H_{eff}C+\tilde{C}H_{eff}C^{(1)} \tag{2.16}$$

$$H_{eff}^{(1)}C+H_{eff}C^{(1)}=CE^{(1)}+C^{(1)}E \tag{2.17}$$

$$\tilde{C}H_{eff}^{(1)}+\tilde{C}^{(1)}H_{eff}=E^{(1)}\tilde{C}+E\tilde{C}^{(1)} \tag{2.18}$$

$$\tilde{C}^{(1)}C+\tilde{C}C^{(1)}=0=C^{(1)}\tilde{C}+C\tilde{C}^{(1)} \tag{2.19}$$

$$H_{eff}^{\nu\mu(1)}=\left\langle \Phi_{\nu}\right| e^{-T_{\mu}}\left\{\hat{H}^{(1)}+[\hat{H},T_{\mu}^{(1)}]\right\} e^{T_{\mu}}\left|\Phi_{\mu}\right\rangle \qquad \forall\mu,\nu \tag{2.20}$$

$$\begin{aligned}\left\langle \Phi_{\mu}^{*}\right| e^{-T_{\mu}}\left\{\hat{H}^{(1)}+[\hat{H},T_{\mu}^{(1)}]\right\} e^{T_{\mu}}\left|\Phi_{\mu}\right\rangle &= \sum_{\nu\neq\mu}\left\langle \Phi_{\mu}^{*}\right| e^{-T_{\mu}}e^{T_{\nu}}\left|\Phi_{\nu}\right\rangle H_{eff}^{\nu\mu(1)} \\ &+ \sum_{\nu\neq\mu}\left\langle \Phi_{\mu}^{*}\right| e^{-T_{\mu}}\left(T_{\nu}^{(1)}-T_{\mu}^{(1)}\right)e^{T_{\nu}}\left|\Phi_{\nu}\right\rangle H_{eff}^{\nu\mu} \qquad \forall\mu\end{aligned} \tag{2.21}$$

To compute first-order response quantities, Eqs (2.20)-(2.21) are to solved first, obtaining $T^{(1)}$ and $H_{eff}^{(1)}$. We manipulate these equations into a form suitable for further discussions. Using normal-ordered expressions for $\hat{H}$ and $\hat{H}^{(1)}$ as in Eq (2.12) and making use of resolution of identity, we can write Eq (2.20) as follows.

$$H_{eff}^{\nu\mu(1)}=Y(\nu,\mu)\bullet T_{\mu}^{(1)}+X(\nu,\mu)\bullet F_{\mu}^{(1)}+W(\nu,\mu)\bullet V^{(1)} \tag{2.22}$$

Here, symbol $\bullet$ denotes dot-product. The quantities Y, X and W are column vectors formed by collecting coefficient of a particular element of $T_{\mu}^{(1)}$ (for Y), $F_{\mu}^{(1)}$ (for X) and $V^{(1)}$ (for W) in Eq (2.20). Column lengths of Y, X and W are equal to number of elements of $T_{\mu}^{(1)}$, $F_{\mu}^{(1)}$ and $V^{(1)}$ respectively. It should be noted that dependence of $H_{eff}^{\nu\mu(1)}$ on left side vacuum Φ_{ν} is limited to quantities Y, X and W. This fact will be useful in next section when Z-vector method is introduced. Eq (2.21) is a coupled inhomogeneous equation in $T_{\mu}^{(1)}$ and can be written as follows.

$$AT^{(1)}=B \tag{2.23}$$

Here, A is a square matrix of size N_T, B and $T^{(1)}$ are column matrices of size N_T, and N_T is the total number of cluster amplitudes in all cluster operators. Matrix A is referred to as the SUMRCC Jacobian. Column matrix $T^{(1)}$ is obtained by juxtaposing cluster amplitude response quantities for all vacuums into a single column. Explicit form for these matrices can be given as follows.

$$\begin{aligned} AT^{(1)} = {} & \langle \Phi^*_\mu | e^{-T_\mu}[\hat{H}, T^{(1)}_\mu] e^{T_\mu} | \Phi_\mu \rangle - \sum_{\nu \neq \mu} \langle \Phi^*_\mu | e^{-T_\mu} \left(T^{(1)}_\nu - T^{(1)}_\mu \right) e^{T_\nu} | \Phi_\nu \rangle H^{\nu\mu}_{eff} \\ & - \sum_{\nu \neq \mu} \langle \Phi^*_\mu | e^{-T_\mu} e^{T_\nu} | \Phi_\nu \rangle \langle \Phi_\nu | e^{-T_\mu}[\hat{H}, T^{(1)}_\mu] e^{T_\mu} | \Phi_\mu \rangle \qquad \forall \mu \end{aligned} \tag{2.24}$$

$$B = \langle \Phi^*_\mu | e^{-T_\mu} \hat{H}^{(1)} e^{T_\mu} | \Phi_\mu \rangle - \sum_{\nu \neq \mu} \langle \Phi^*_\mu | e^{-T_\mu} e^{T_\nu} | \Phi_\nu \rangle \langle \Phi_\nu | e^{-T_\mu} \hat{H}^{(1)} e^{T_\mu} | \Phi_\mu \rangle \tag{2.25}$$

where expression for $H^{(1)}_{eff}$ as in Eq (2.20) has been used. Further simplification requires the use of normal-ordered form for $\hat{H}$ and $\hat{H}^{(1)}$ along with associated diagrammatic techniques. Diagrammatic expressions for Eq (2.24) can be obtained from diagrammatic expressions for SUMRCC cluster amplitude equations[16] by replacement of occurrence of a single T-vertex with a single $T^{(1)}$-vertex in all possible ways. It is important to note that SUMRCC Jacobian matrix A is perturbation independent and depends only on zeroth-order quantities T_μ and $\hat{H}$.

Inhomogeneous term B, although depends on perturbation $\hat{H}^{(1)}$, does not depend on first-order response quantity $T^{(1)}$. Using normal-ordered expression for $\hat{H}^{(1)}$ as in Eq (2.12), B can be simplified into the following form.

$$B = DF^{(1)} + GV^{(1)} \tag{2.26}$$

Here, D and G are rectangular matrices with same number of rows as B and A. $F^{(1)}$ is a column matrix obtained by juxtaposing all one-body matrix elements $F^{(1)}_N(\mu)$ for all vacuums, and $V^{(1)}$ is a column matrix of all two-body matrix elements $V^{(1)}_N$. As in the case of Jacobian, matrices D and G are independent of perturbation and depend only on zeroth-order quantities T_μ and H. The perturbative proof of J&M can be extended to Eqs (2.24)-(2.25) and lead to fully connected expressions for $T^{(1)}$ and $H_{eff}^{(1)}$.

Once $H_{eff}^{(1)}$ is obtained by solving Eq (2.25), it can be used in Eqs (2.16)-(2.19) to calculate other first-order quantities $E^{(1)}$, $C^{(1)}$ and $\tilde{C}^{(1)}$. For computation of $E^{(1)}$, it is not necessary to compute $C^{(1)}$ and $\tilde{C}^{(1)}$. As in coupled-perturbed type of treatments, writing $C^{(1)} = CU$ (solving for U is equivalent to solving for $C^{(1)}$) and deriving $\tilde{C}^{(1)} = -U\tilde{C}$ from Eq (2.19), the following expression can be obtained for $E^{(1)}$.

$$E^{(1)} = \tilde{C}H_{eff}^{(1)}C + EU - UE \tag{2.27}$$

The diagonal elements of Eq (2.27) determine first-order response of energy for different states, and it is easy to see that they are independent of U and hence also independent of $C^{(1)}$ and $\tilde{C}^{(1)}$. Non-diagonal elements o Eq (2.27) determine the non-diagonal elements of U. The diagonal elements of U can are determined by some other auxiliary conditions.

II.4 Z-vector method for SUMRCC theory

From the previous section, it is clear that first-order energy response depends explicitly on first-order response of non-stationary parameters such as T and molecular or atomic orbitals. This necessitates solution of as many first-order response equations for these quantities as the number of modes of perturbation. Although this may be manageable for molecular electronic properties where there are only three independent perturbations, it becomes highly tedious when gradient computations are considered, especially when the number of atoms in the molecule increases or when the molecule is less symmetric.

In the SRCC context, Adamowicz, Fitzgerald, Salter, Bartlett and coworkers[7,28-29] have shown that this procedure can be obviated by replacing the set of first-order cluster amplitude response equations for different modes of perturbation by a new single perturbation-independent equation involving a new quantity referred to as Z-vector. With this, computation of first-order energy response reduces to solving for this perturbation-independent quantity followed by its scalar product with a perturbation-dependent quantity that does not depend on first-order response quantities. This method is similar in spirit to the generalized Hellmann-Feynman variational (or stationary) theories,[30] and is referred to as the Z-vector method. It was first introduced by Handy and Schaefer[8] in their study concerning orbital response corrections to CI analytic energy derivatives, and can be traced back to the interchange theorem of Dalgarno and Stewart.[31] Fitzgerald, Salter and coworkers[29] have carried out further simplifications of SRCC gradients by incorporating orbital response and compactly rewriting the energy gradients as scalar contraction of effective one-body and two-body CC density matrices with molecular orbital integral derivatives.

For the SUMRCC theory, extension of the Z-vector method requires elimination of first-order cluster amplitude response quantities $T^{(1)}$ present in the first term of Eq (2.27) in lieu of a perturbation independent Z-vector. The diagonal elements of this equation are nothing but first-order energy response quantities $E^{(1)}$ and can be written as follows.

$$E_{I,I}^{(1)} = E_I^{(1)} = \sum_{\mu,\nu} \tilde{C}_\nu^I H_{eff}^{\nu\mu(1)} C_\mu^I \qquad (2.28)$$

Here, label I denotes a particular state whose energy response is sought. Using Eq (2.22), this can be simplified to,

$$E_I^{(1)} = \sum_{\mu} C_{\mu}^I \left[Y_{\mu}^I \bullet T_{\mu}^{(1)} + X_{\mu}^I \bullet F_{\mu}^{(1)} + W_{\mu}^I \bullet V^{(1)} \right] \tag{2.29}$$

In the above Eq, quantities Y_{μ}^I, X_{μ}^I and W_{μ}^I are defined by a generic expression $G_{\mu}^I = \sum_{\nu} \tilde{C}_{\nu}^I G(\nu, \mu)$. Juxtaposition of column vectors $C_{\mu}^I G_{\mu}^I$, $T_{\mu}^{(1)}$ and $F_{\mu}^{(1)}$ for different vacuums into single column vectors G^I, $T^{(1)}$ and $F^{(1)}$ respectively, leads to,

$$E_I^{(1)} = Y^I \bullet T^{(1)} + X^I \bullet F^{(1)} + W^{(I)} \bullet V^{(1)} \tag{2.30}$$

In the above expression, the state-dependency in each term has been completely restricted to only one quantity (on left hand side) of dot product. Since $T^{(1)}$ is an excitation operator, Y^I can be thought of as a de-excitation operator. Eq (2.30) along with cluster amplitude response Eq (2.23) forms a basis for generalization of Z-vector method into SUMRCC. Eq (2.23) can be solved for $T^{(1)}$, and substituted into first term of Eq (2.30) to give,

$$E_I^{(1)} = Y^I \bullet \left[A^{-1} B \right] + X^I \bullet F^{(1)} + W^{(I)} \bullet V^{(1)} \tag{2.31}$$

Defining a de-excitation quantity Z-vector Z^I by,

$$Y^I = Z^I A \tag{2.32}$$

Eq (2.31) can be rewritten as,

$$E_I^{(1)} = Z^I \bullet B + X^I \bullet F^{(1)} + Q^{(I)} \bullet V^{(1)} \tag{2.33}$$

The above two Eqs (2.32)-(2.33) are results of generalization of the Z-vector method for SUMRCC theory. In contrast to cluster amplitude response Eq (2.23), the Z-vector equation Eq (2.32) is easily seen to be perturbation independent (because A and

Y^I are perturbation independent) and needs to be solved only once. As mentioned earlier, this represents a significant computational advantage for calculating first-order molecular properties using SUMRCC.

Using Eq (2.26) for B and combining common terms, Eq (2.33) can be further simplified by introducing one-body and two-body effective CC density matrices Γ_1^I and Γ_2^I.

$$E_I^{(1)} = \Gamma_1^I \bullet F^{(1)} + \Gamma_2^I \bullet V^{(1)} \tag{2.34}$$

$$\Gamma_1^I = X^I + Z^I D \tag{2.35}$$

$$\Gamma_1^I = A^I + Z^I G \tag{2.36}$$

These effective CC density matrices suitably generalize the ones used in SRCC by Fitzgerald, Salter and coworkers.[29] These equations form a basis for efficient expressions to computing first-order molecular properties and gradients using SUMRCC. Such properties can be expressed as a full contraction of (or trace of the product of) an effective density operator and derivative molecular orbital integrals. It should be noted that the Z-vector obtained by solving Eq (2.32) is state-dependent (it carries a label I as a superscript to indicate this fact). This state-dependency comes from quantity Y which is also state-dependent. As a result, effective CC density matrices also become state-dependent. However, they are all perturbation-independent quantities and are the same for all modes of perturbation, which is the basic goal of the Z-vector method.

Diagrammatic evaluation of effective density matrices is easily carried out using diagrammatic expressions for products $Z^I D$ and $Z^I G$. The state independence of D and G facilitates this, particularly when computations are carried out on many states at a time.

Therefore, evaluation of first-order molecular properties and gradients for a particular state in SUMRCC theory can be carried out by first determining the Z-vector associated with that state, constructing effective SUMRCC density matrices for that state, and finally performing their scalar contraction with corresponding perturbation dependent quantities $F^{(1)}$ and $V^{(1)}$. Following Rice and Amos[32], this contraction can be efficiently carried out in AO basis which is computationally convenient and avoids multiple four-index transformations of integral derivatives from atomic orbital to molecular orbital basis.

II.5 State-independent Z-vector method

An analysis of Z-vector equations presented in previous section reveals some interesting aspects which arise due to multi-state nature of the theory. As already noted, Z-vector is not universal for all states of the quasi-degenerate manifold considered and it becomes state-dependent. This fact has been observed in EOM-CC[33] as well, which is also a multi-state theory. The size of Z-vector for each state is equal to the total number of cluster amplitudes for all vacuums, N_T. In other words, the size of Z-vector for each state is equal to the number of independent wave-function parameters whose response is to be eliminated from the first-order energy response. Therefore, the total size of Z-vectors required for all states in the manifold scales linearly with dimension of the model space.

In effective Hamiltonian based MRCC theories, wave functions and energies of all the states within the quasi-degenerate manifold are simultaneously obtained using a single set of cluster amplitudes. Therefore, it is natural to enquire if the first-order response of all the states within the manifold can be summarized with a single state-independent Z-vector. Furthermore, it is desirable to have a state-independent Z-vector whose size is same as the size of all cluster amplitudes T.

It is clear from Eq (2.27) that a state-independent Z-vector is possible if the first-order response of cluster amplitude can be eliminated directly from the first-order response of effective Hamiltonian (which is state-independent). Recently, Ajitha and Pal[34] have attempted to generalize the Z-vector method for VUMRCC theory. Their approach, although proved to be unsuccessful, is essentially based on this idea except that they implicitly look for an elimination which leads to state-independent Z-vector of the same size as cluster amplitudes. Our recent analysis shows that it is not possible to construct a state-independent Z-vector in above sense.[35]

However, an alternative procedure may be visualized by carrying out elimination for each matrix element of $H_{eff}^{(1)}$. The column matrix $T_{\mu}^{(1)}$ in the first term of Eq (2.22) can be formally expressed in terms of column matrix $T^{(1)}$ by introducing a projection matrix P_{μ} of compatible dimension.

$$T_{\mu}^{(1)} = P_{\mu} T^{(1)} \tag{2.37}$$

As in previous section, Eq (2.23) can be formally solved for $T^{(1)}$ and substituted into first term of Eq (2.22). After rearrangement this leads to following Z-vector equations.

$$H_{eff}^{\nu\mu(1)} = Z(\nu,\mu) \bullet B + X(\nu,\mu) \bullet F_{\mu}^{(1)} + W(\nu,\mu) \bullet V^{(1)} \tag{2.38}$$

$$Z(\nu,\mu) A = Y(\nu,\mu) P_{\mu} \tag{2.39}$$

Now, we have M^2 Z-vectors $Z(\nu,\mu)$ each of size same as cluster amplitudes. These Z-vectors are universal for all states unlike state-dependent Z-vectors of previous section. However, total number of parameters in these M^2 state-independent Z-vectors is even higher than the total number of state-dependent Z-vectors for the entire quasi-degenerate manifold. Using linear independence of model space determinants, it can be easily shown that these M^2 vectors $Y(\nu,\mu)P_\mu$ are linearly independent. Since, SUMRCC Jacobian matrix A is assumed to be invertible, it follows that M^2 Z-vectors $Z(\nu,\mu)$ are also linearly independent. These Z-vectors can be used for efficient computation of matrix elements of compute $H_{eff}^{(1)}$. Expression for $H_{eff}^{(1)}$ in terms of these Z-vectors as in Eq (2.38) can be substituted into Eq (2.27) leading to a new set of equations, which can be used to obtain energy response quantities of interest.

Clearly, these state-independent M^2 Z-vectors contain much more information than is necessary for computing first-order energy response quantities. Therefore, this procedure is inefficient for computing these quantities. Until now, we have concentrated on the diagonal elements of Eq (2.27). The off-diagonal elements are not required if interest lies only in first-order energy response quantities. For higher-order response properties, full solution of Eq (2.27) is necessary and one may think that state-independent Z-vectors may be useful in such cases. But then, solution of $T^{(1)}$ for each mode of perturbation is also necessary in such cases, and hence elimination of $T^{(1)}$ in $H_{eff}^{(1)}$ seems to be really not necessary (although it may prove advantageous). As will be seen in third chapter, computation of higher-order energy response properties for a specific state can be carried out using a constrained variation approach. Therefore, the idea of M^2 state-independent Z-vectors seems to be of no significant use for higher-order energy response properties as well, even when all states are considered simultaneously. Nonetheless, the idea is interesting and may lead to some future theoretical methods based on full stationarity of effective Hamiltonian. In addition, for transition properties, it is possible that they have some useful role to play.

II.6 Conclusions

In recent times, effective Hamiltonian based MRCC theories, especially the VUMRCC variant, are being applied to compute first-order molecular properties of open shell radicals and excited states of several molecules. These calculations do not include the benefits of Z-vector method. The state-dependent Z-vector method described in fourth section is useful in simplifying these calculations. The state-dependency of Z-vector, although somewhat surprising, is a consequence of multi-state nature of MRCC theories. Its implications will be pursued in future chapters.

References

1. I. Lindgren and D. Mukherjee, Phys. Rep. **151**, 93 (1987)
2. D. Mukherjee and S. Pal, Adv. Quant. Chem. **20**, 292 (1989)
3. J. Paldus, in Methods in Computational Molecular Physics, NATO ASI Series B, edited by S. Wilson and G. H. F. Dierckson (Plenum, New York, 1992) p99
4. (a) R. Mattie, M. Rittby, R. J. Bartlett, and S. Pal, in *Aspects of many-body effects in molecules and extended systems, Lecture notes in Chemistry,* edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p143 (b) U. Kaldor, in same volume, p154
5. (a) J. Paldus, L. Pylypow and B. Jezioroski, in *Many-body methods in Quantum Chemistry, Lecture notes in Chemistry,* edited by U. Kaldor (Springer-Verlag, 1989) Vol.**52**, p151 (b) J. Paldus, P. Piecuch, B. Jezioroski, and L. Pylypow, in *Recent Advances in Many-Body Theories*, edited by T. L. Ainsworthy, C. E. Campbell, B. E. Clements, and E. Krotschek (Plenum, New York, 1992), Vol.**3**, p287
6. L. Meissner, K. Jankowski and J. Wasilewski, Int. J. Quant. Chem. **34**, 535 (1888)
7. R. J. Bartlett, in *Geometrical Derivatives of Energy Surface and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht,1986), p35

8. N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984)

9. H. Koch, H. J. A. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria, H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990)

10. H. J. Monkhorst, Int. J. Quantum Chem. Quantum Chem. **S11**, 421 (1977)

11. S. Pal, Phys. Rev. **A39**, 39 (1989)

12. B. Jezioroski and H. J. Monkhorst, Phys. Rev. **A24**, 1668 (1982)

13. H. Silverstone and Sinanoglu, J. Chem. Phys. **44**, 1899, 3608 (1966)

14. B. Brandow, Rev. Mod. Phys. **39**, 771 (1967)

15. (a) G. Hose and U. Kaldor, J. Phys. **B12**, 3827 (1979) (b) Phys. Scripta. **21**, 357 (1980)

16. S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **95**, 8227 (1991)

17. (a) B. Jezioroski and J. Paldus, J. Chem. Phys. **88**, 5673 (1988) (b) J. Paldus, P. Piecuch, L. Polypow, and B. Jezioroski, Phys. Rev. **A47**, 2738 (1993) (c) P. Piecuch and J. Paldus, Phys. Rev. **A49**, 3479 (1994) (d) P. Piecuch and J. Paldus, Theor. Chim. Acta. **83**, 69 (1992) (e) P. Piecuch and J. Paldus, J. Chem. Phys. **101**, 5875 (1994)

18. A. Balkova, S. A. Kucharski, L. Meissner, and R. J. Bartlett, Theor. Chim. Acta. **80**, 335 (1991)

19. A. Balkova, S. A. Kucharski, and R. J. Bartlett, Chem. Phys. Lett. **182**, 511 (1991)

20. (a) S. Berkovic and U. Kaldor, Chem. Phys. Lett. **199**, 42 (1992) (b) S. Berkovic and U. Kaldor, J. Chem. Phys. **98**, 3090 (1993)

21. L. Meissner, S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **91**, 6187 (1989)

22. L. Meissner and R. J. Bartlett, J. Chem. Phys. **92**, 561 (1990)

23. A. Balkova, S. A. Kucharski, L. Meissner, and R. J. Bartlett, J. Chem. Phys. **95**, 4311 (1991)
24. S. A. Kucharski, A. Balkova, P.G. Szalay, and R. J. Bartlett, J. Chem. Phys. **97**, 4289 (1992)
25. A. Balkova and R. J. Bartlett, J. Chem. Phys. **99**, 7907 (1993); **101**, 4936 (1994); **102**, 7116 (1995)
26. S. Berkovic and U. Kaldor, J. Chem. Phys. **98**, 3090 (1993)
27. P. G. Szalay, Int. J. Quantum Chem. **55**, 151 (1995)
28. L. Adamowicz, W. D. Laidig, and R. J. Bartlett, Int. J. Quant. Chem. **S18**, 245 (1984)
29. (a) G. Fitzgerald, R. J. Harrison, and R. J. Bartlett, J. Chem. Phys. **85**, 5143 (1986) (b) E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989)
30. S. T. Epstein, *The Variation Principle in Quantum Chemistry*, (Academic, New York, 1974).
31. A. Dalgarno and A. L. Stewart, Proc. R. Soc. London, Ser. **A 238**, 269 (1957)
32. J. E. Rice and R. D. Amos, Chem. Phys. Lett. **122**, 585 (1985)
33. J. F. Stanton, J. Chem. Phys. **99**, 8840 (1993)
34. D. Ajitha and S. Pal, J. Chem. Phys. **111**, 3832 (1999); **111**, 9892(E) (1999)
35. K. R. Shamasundar, S. Asokan, and S. Pal. J. Chem. Phys. **120**, 6381 (2004)

Chapter III

Constrained variation approach and its application to higher-order energy response properties using state-universal MRCC theory

III.1 Introduction

Electronic structure methods where a stationarity condition on an energy functional with respect to complete variation of the functional is used to define parameters of electronic wave-function are known as variational theories.[1] Sometimes they are referred to as stationary theories in order to distinguish them from variational theories where the energies obtained satisfy the upper-bound property. The word variation in quantum chemistry, especially in earlier days, has been tied down to the existence of this upper-bound property. In this work, variation is used in its general sense. Variational theories are known to have certain interesting properties which can be used to simplify computation of molecular properties. These theories obey the generalized Hellmann-Feynman theorem (GHFT) and $(2n+1)$ rule.[1] This rule represents a generalization of GHFT for higher-order properties. It states that the knowledge of response of variationally determined wavefunction parameters up to order n is sufficient to obtain the expressions for energy response quantities up to order $(2n+1)$.

The effective Hamiltonian based MRCC theories being considered here do not obey the GHFT or the $(2n+1)$ rule. Consequently, evaluation of molecular properties in such theories is somewhat difficult as compared to variational theories. For computation of first-order properties using MRCC theories, the state-dependent Z-vector method presented in the previous chapter effectively alleviates these difficulties. While the GHFT proves that first-order response of variationally obtained wave-function parameters is not necessary for computation of first-order properties, the Handy-Schaefer Z-vector method[2] proves that the seemingly necessary first-order response of non-variationally determined wavefunction parameters can be eliminated by introducing a new perturbation-independent quantity, namely the Z-vector. Therefore, Z-vector method may be thought of as some kind of analogue of GHFT for non-variational methods. Based on this analogy, some simplifications similar to the $(2n+1)$ rule may be expected for higher-order properties. However, it is not easy to extend Z-vector type of benefits for higher-order properties by adhering to Handy-Schaefer elimination technique. Although such an extension has been worked out by Salter and Bartlett[3] for second-order properties in SRCC, it is still somewhat cumbersome.

A conceptually different route was taken by Helgaker, Koch, Jorgensen and coworkers[4-8] who pursued an alternative formulation of SRCC energy derivatives which automatically incorporates Z-vector like benefits to all orders. It is based on the method of undetermined Lagrange multipliers and is also referred to as constrained variation approach (CVA). This approach embeds Z-vector method as a simple zeroth-order result. The hierarchical structure of response equations becomes clear in this approach and a new $(2n+2)$ rule for undetermined Lagrange multipliers emerges.[5-7]

In this chapter, after a brief discussion on CVA for SRCC, we formulate a functional for SUMRCC which directly leads to the state-dependent Z-vector method derived in the previous chapter. We compare the present functional with the one used by Szalay[9] in his studies on relative cost of MRCC gradient computations, and identify a certain degree of freedom in the choice of functional. Using time-independent response approach based on the proposed functional, generic expression for up to third-order molecular properties in SUMRCC are derived. This illustrates advantages of state-dependent constrained variation approach for computation of higher-order molecular properties.

III.2 Constrained variation approach for SRCC

Constrained variation approach (CVA) for SRCC was proposed by Helgaker and Jorgensen.[4-6] The basic idea is to construct a new functional $\mathcal{J}$ based on the standard non-variational SRCC energy expression with undetermined Lagrange multipliers $\Lambda = \{\lambda_q, \forall q\}$ corresponding to the standard non-variational SRCC equations as constraints.[7] Denoting the collection of all cluster amplitudes T and Lagrange multipliers Λ by $\boldsymbol{\Theta} = \{T, \Lambda\}$, the functional can be written as follows.

$$\mathcal{J}(\boldsymbol{\Theta}) = \langle \Phi_0 | e^{-T} \hat{H} e^{T} | \Phi_0 \rangle + \sum_{q \neq 0} \lambda_q \langle \Phi_q | e^{-T} \hat{H} e^{T} | \Phi_0 \rangle \qquad (3.1)$$

Here, $\{\Phi_q, \forall q \neq 0\}$ are the excited determinants generated by the action of cluster operator $T = \sum_q t_q \tau_q$ on the vacuum Φ_0. The operator τ_q is the excitation operator generating $|\Phi_q\rangle = \tau_q |\Phi_0\rangle$. In CVA, this functional is made fully stationary with respect to all variations in parameters $\boldsymbol{\Theta}$.

$$\frac{\delta \mathcal{J}(\boldsymbol{\Theta})}{\delta \boldsymbol{\Theta}} = 0 \qquad (3.2)$$

When variations with respect to Lagrange multipliers λ_q are considered in Eq (3.2), we get back the SRCC cluster amplitude equations.

$$\langle \Phi_q | e^{-T} \hat{H} e^{T} | \Phi_0 \rangle = 0 \quad \forall \Phi_q \qquad (3.3)$$

When variations with respect to SRCC cluster amplitudes t_q are considered in Eq (3.2), we get the following equations which define the Lagrange multipliers.

$$\langle \Phi_0 | e^{-T}[\hat{H},\tau_p]e^{T} | \Phi_0 \rangle + \sum_{q \neq 0} \lambda_q \langle \Phi_q | e^{-T}[\hat{H},\tau_p]e^{T} | \Phi_0 \rangle = 0 \quad \forall \Phi_p \tag{3.4}$$

By defining Λ as a column vector containing all Lagrange multipliers $\left\{ \lambda_q, \forall q \neq 0 \right\}$, Y as another column vector $\left\{ \langle \Phi_0 | e^{-T}[\hat{H},\tau_p]e^{T} | \Phi_0 \rangle \quad \forall p \right\}$, and A as SRCC Jacobian matrix $A_{qp} = \langle \Phi_q | e^{-T}[\hat{H},\tau_p]e^{T} | \Phi_0 \rangle \ \forall q,p$, the above equation can be written as follows.

$$\Lambda^T A + Y^T = 0 \tag{3.5}$$

This is just the SRCC Z-vector equation[10] with Lagrange multipliers Λ taking the place of Z-vector. The value of the functional at the stationary point where Eq (3.3)-(3.5) are satisfied is just equal to the SRCC energy $E = \langle \Phi_0 | e^{-T}\hat{H}e^{T} | \Phi_0 \rangle$. Therefore, making the functional in Eq (3.1) stationary is completely equivalent to SRCC theory along with corresponding SRCC Z-vector method. In other words, the SRCC theory and the associated Z-vector method have been merged into a single procedure of finding stationary points of a functional. The spirit of CVA is similar to that of stationary or variational theories, namely making a functional stationary to derive working equations. In essence, CVA for SRCC may be viewed as a stationary (or variational) reformulation of the standard SRCC theory.

When the SRCC equations Eq (3.3) are satisfied, the value of the functional is equal to the SRCC energy irrespective of the value of Lagrange multipliers. This means that Lagrange multipliers need not be determined for calculating the value of functional at stationary point (hence the name undetermined). This is equivalent to the fact that SRCC

Z-vector is not needed to compute SRCC energies. However, Lagrange multipliers or Z-vector start to become necessary when energy first derivatives are considered.

The advantage of combining SRCC and the associated Z-vector method into a single functional optimization procedure becomes clear when energy derivatives are considered. Koch, Helgaker, Jorgensen and coworkers[7] have considered energy derivatives in SRCC by applying time-independent analytic response approach to the constrained variation functional. Their analysis reveals that cluster amplitude response quantities, due to stationarity condition, obey the usual $(2n+1)$ rule. The Lagrange multiplier response quantities, due to stationarity as well as due to linear appearance of Lagrange multipliers within the functional, are shown to obey the $(2n+2)$ rule.[5-7]

Jorgensen and coworkers have brought out several interesting properties obeyed by hierarchies of response equations deriving using CVA. For example, they have shown that equations for Lagrange multiplier response quantities and cluster amplitudes response quantities, for any order, share the same SRCC Jacobian.[7] They have used CVA to derive the expressions for gradients and hessians for SRCC and MBPT theories, and efficiently implement them.

Inclusion of orbital response effects is also straightforward within CVA. This can be done by adding into the original functional, some additional terms with Lagrange multipliers corresponding to conditions defining orbitals. This procedure leads to further hierarchy of response equations and has been analyzed in detail by Jorgensen and coworkers.[7]

III.3 Constrained variation approach for state-universal MRCC

In this section, we formulate a constrained variation functional for SUMRCC theory which includes the state-dependent Z-vector method of previous chapter as a zeroth-order result. As in SRCC, this is done by associating a Lagrange multiplier with SUMRCC equations. Since Z-vector is state-dependent, resulting constrained variation functional is expected to be state-dependent.

Before providing explicit expression for the desired Lagrangian functional which combines SUMRCC theory with its state-dependent Z-vector method, the following abbreviations are assumed. The SUMRCC cluster amplitude equation Eq (2.6) is rewritten as follows.

$$\begin{aligned}\mathcal{W}_q(\mu) = \langle \Phi_q(\mu) | e^{-T_\mu} \hat{H} e^{T_\mu} | \Phi_\mu \rangle \\ - \sum \langle \Phi_q(\mu) | e^{-T_\mu} e^{T_\nu} | \Phi_\nu \rangle H_{eff}^{\nu\mu} = 0 \ \ \forall q, \mu\end{aligned} \tag{3.6}$$

$$H_{eff}^{\nu\mu} = \langle \Phi_\nu | e^{-T_\mu} \hat{H} e^{T_\mu} | \Phi_\mu \rangle \tag{3.7}$$

As in the previous chapter, we denote the set of cluster amplitudes for all vacuums by T, the set of all right-side (left-side) model space coefficients for I-th state by C^I ($\tilde{C}^I$), and the set of all Lagrange multipliers corresponding to SUMRCC cluster amplitude equations by Λ. Further, the set of quantities T, C^I, $\tilde{C}^I$, Λ and energy E_I of I-th state (the Lagrange multiplier corresponding to biorthonormality conditions) are collectively denoted by $\mathbf{\Theta}$. The following equations summarize these abbreviations.

$$T = \left\{ T_\mu \ \ \forall \mu \right\} \tag{3.8.1}$$

$$C^I = \left\{ C_\mu^I \ \ \forall \mu \right\} \tag{3.8.2}$$

$$\tilde{C}^I = \left\{ \tilde{C}_\mu^I \ \ \forall \mu \right\} \tag{3.8.3}$$

$$\Lambda = \left\{ \Lambda_\mu \ \ \forall \mu \right\} \tag{3.8.4}$$

$$\mathbf{\Theta} = \left\{ T, \Lambda, C^I, \tilde{C}^I, E_I \right\} \tag{3.8.5}$$

With these abbreviations, the SUMRCC constrained variational functional can be compactly expressed as follows.

$$\mathcal{J}(\Theta) = \sum_{\mu,\nu} \tilde{C}_{\nu}^{I} H_{eff}^{\nu\mu} C_{\mu}^{I} + \sum_{q,\eta} \lambda_q(\eta) \mathcal{W}_q(\mu) - E_I \left(\sum_{\mu} \tilde{C}_{\mu}^{I} C_{\mu}^{I} - 1 \right) \tag{3.9}$$

The functional is state-dependent and this enters through first and third term in the functional. The stationarity of this functional with respect to first-order variations in variables $\Theta = \left\{ T, \Lambda, C^{I}, \tilde{C}^{I}, E_I \right\}$ is expressed as in Eq (3.2). When variations with respect to Lagrange multipliers of a specific vacuum are considered, as usual the SUMRCC equations for the vacuum are recovered. Variations with respect to model space coefficients lead to corresponding eigenvalue equations Eq (2.8)-(2.9) and variation with respect to E_I leads to corresponding biorthogonality condition Eq (2.11). Variations with respect to cluster amplitudes lead to the following equations for the Lagrange multipliers.

$$\sum_{q,\eta} \lambda_q(\eta) \left[\mathcal{W}_q(\mu) \right]_{\tau_l(\mu)} = -\sum_{\nu} \tilde{C}_{\nu}^{I} C_{\mu}^{I} \left[H_{eff}^{\nu\mu} \right]_{\tau_l(\mu)} \quad \forall l, \mu \tag{3.10}$$

Here, subscript $\tau_l(\mu)$ denotes differentiation of the expression in square brackets with respect to a specific cluster amplitude $t_l(\mu)$, and $\tau_l(\mu)$ is the hole-particle excitation operator which generates $\Phi_l(\mu)$ when acting on its vacuum Φ_μ. These equations are identical to the state-dependent Z-vector equations of the previous chapter with Lagrange multipliers playing the role of Z-vector. The quantity within square brackets on the left hand side of Eq (3.10) can be identified to be the SUMRCC Jacobian matrix A of previous chapter. Therefore, the functional in Eq (3.9) leads to state-dependent Z-vector method. It will be used in next section to derive generic expression for up to third-order molecular properties.

There is a degree of freedom in the choice of the functional which needs some discussion. Szalay has employed CVA in his studies on relative cost of MRCC gradients. The following functional has been proposed in his work.[9]

$$\mathcal{J}(\Theta)=\sum_{\mu,\nu}\tilde{C}^I_\nu H^{\nu\mu}_{eff}C^I_\mu+\sum_{q,\eta}\tilde{C}^I_\eta C^I_\eta\lambda_q(\eta)\mathcal{W}_q(\mu)-E_I\left(\sum_{\mu}\tilde{C}^I_\mu C^I_\mu-1\right) \tag{3.11}$$

This functional differs from the functional in (3.9) by containing state-dependency in the second term. With this, all terms of the functional has been made explicitly state-dependent. By applying requisite variations, it can be shown that this functional leads to the following equations for Lagrange multipliers.

$$\sum_{q,\eta}\lambda_q(\eta)\left[\tilde{C}^I_\eta\mathcal{W}_q(\mu)C^I_\eta\right]_{\tau_l(\mu)}=-\sum_{\nu}\tilde{C}^I_\nu C^I_\mu\left[H^{\nu\mu}_{eff}\right]_{\tau_l(\mu)}\quad\forall l,\mu \tag{3.12}$$

While the right hand side of Eq (3.12) is same as in Eq (3.10), the left hand side is now explicitly state-dependent. In particular, the SUMRCC Jacobian becomes state-dependent. The Eq (3.12) is not same as the SUMRCC Z-vector equation. Therefore, the resulting Lagrange multipliers will be different. However, molecular properties or gradients will have to be same in either of these approaches. This is ensured by compensating changes in first-order molecular property expressions obtained using these functionals.

From the above considerations, it is clear that there are many possible functionals which lead to different equations for Lagrange multipliers. Choosing a specific functional is equivalent to choosing a specific Jacobian matrix entering the Lagrange multiplier equations. Although such a possibility exists even in SRCC, it can be easily seen to lead to solutions which are trivially different from each other. In MRCC theories, the situation is clearly different.

The functional in Eq (3.9) is unique in some sense. It is the only one which leads to a state-independent Jacobian matrix in Lagrange multiplier. All other functionals lead to state-dependent Jacobian. Further, in the next section it will be clear that the functional in Eq (3.9) is the only one which leads to same Jacobian entering the response equations for cluster amplitudes and Lagrange multipliers. All other functionals lead to some kind of asymmetry. Although making the Jacobian to be state-dependent as in Eq (3.12) seems to be not necessary, it may lead to advantageous expressions for individual components of effective SUMRCC density matrices to bear some similarity to their SRCC counterparts.

III.4 Higher-order molecular properties in state-universal MRCC

As mentioned before, the advantages of CVA over the Z-vector method become evident for higher-order properties. In this section, time-independent analytic response approach is applied for the functional in Eq (3.9). The first-order response equations for $\mathbf{\Theta}$ are presented and connection with the results of Jorgensen and coworkers[7] for SRCC is made. Using the $(2n+1)$ rule for cluster amplitudes and model space coefficients and the $(2n+2)$ rule for Lagrange multipliers, simple generic expressions for properties up to third-order are obtained.

As in the previous chapter, in presence of a weak external perturbation $\hat{H}^{(1)}$ of strength g added into the Hamiltonian $\hat{H}$ to yield $\hat{H}(g)=\hat{H}+g\hat{H}^{(1)}$, the constrained variation functional becomes perturbation dependent and is written as $\mathcal{J}(g,\mathbf{\Theta})$. Response equations can be obtained in two different but equivalent approaches. In the first approach followed by Jorgensen and coworkers[7] as well as Bartlett and coworkers[10], the functional $\mathcal{J}(g,\mathbf{\Theta})$ and the stationary equations are expanded as a Taylor series in strength parameter g. Terms of same order in g in $\boldsymbol{\Theta}$ equations are collected to obtain hierarchical equations for various response quantities $\boldsymbol{\Theta}^{(n)}$. The second approach, followed by Pal[11] in the context of variational coupled-cluster theories, derives the response equations of any required order as stationary equations. The functional $\mathcal{J}(g,\boldsymbol{\Theta})$ is expanded as,

$$\mathcal{J}(g,\boldsymbol{\Theta}) = \mathcal{J}^{(0)} + g\mathcal{J}^{(1)} + \tfrac{1}{2!}g^2\mathcal{J}^{(2)} + \cdots \tag{3.13}$$

Here, $\mathcal{J}^{(n)}$ is a functional of quantities $\left\{\boldsymbol{\Theta}^{(m)}\ m=0,n\right\}$. All the response equations up to a required order n can be derived by making functionals $\left\{\mathcal{J}^{(k)}\ k=0,n\right\}$ stationary with respect to $\left\{\boldsymbol{\Theta}^{(m)}\ m=0,k\right\}$. This leads to the following equations.

$$\frac{\delta\mathcal{J}^{(k)}}{\delta\boldsymbol{\Theta}^{(m)}} = 0 \quad \forall k = 1,n \quad \forall m \le k \tag{3.14}$$

This includes the $n=0$ case corresponding to unperturbed (zeroth-order) equations as well. Henceforth, we drop the superscript for zeroth-order quantities. It has been shown that there is a large amount of redundancy in the above equations.[11] Therefore, it is sufficient to solve the following set of equations.

$$\frac{\delta\mathcal{J}^{(m)}}{\delta\boldsymbol{\Theta}} = 0 \quad \forall m = 0,n \tag{3.15}$$

This procedure leads to a set of hierarchical equations for $\left\{\boldsymbol{\Theta}^{(m)}\ m=0,n\right\}$. It should be pointed out that both the approaches are entirely equivalent and either of them may be used to derive the response equations. In this work, we follow the second approach. To obtain the expressions for up to third-order properties, the response quantities $\boldsymbol{\Theta}$ and $\boldsymbol{\Theta}^{(1)}$ are necessary. For this, Eq (3.15) has to be solved up to $n=1$.

III.4.1 First-order response equations

We have chosen the functional in Eq (3.9) for deriving response equations. The zeroth-order equations are obtained from Eq (3.15) when $m = 0$. The resulting equations, i.e., Eq (3.10) have already been discussed in the previous section. The first order response quantities can be obtained by,

$$\frac{\delta \mathcal{J}^{(1)}}{\delta \boldsymbol{\Theta}} = 0 \tag{3.16}$$

For different parameters in $\boldsymbol{\Theta}$, the above equations lead to following equations for $\boldsymbol{\Theta}^{(1)}$. These equations depend on all zeroth-order quantities $\boldsymbol{\Theta}$.

$$\sum_{q,\eta} \left[\mathcal{W}_l(\mu)\right]_{\tau_q(\eta)} t_q^{(1)}(\eta) = - \left[\mathcal{W}_l(\mu)\right]_{\hat{H}\to\hat{H}^{(1)}} \quad \forall l, \mu \tag{3.17}$$

$$\sum_{\mu} C_\mu^{I(1)} H_{eff}^{\nu\mu} + \sum_{\mu} C_\mu^I H_{eff}^{\nu\mu(1)} = E_I^{(1)} C_\nu^I + E_I C_\nu^{I(1)} \quad \forall \nu \tag{3.18}$$

$$\sum_{\nu} \tilde{C}_\nu^{I(1)} H_{eff}^{\nu\mu} + \sum_{\nu} \tilde{C}_\nu^I H_{eff}^{\nu\mu(1)} = E_I^{(1)} \tilde{C}_\mu^I + E_I C_\mu^{I(1)} \quad \forall \mu \tag{3.19}$$

$$\sum_{\mu} \left(\tilde{C}_\mu^{I(1)} C_\mu^I + \tilde{C}_\mu^I C_\mu^{I(1)} \right) = 0 \tag{3.20}$$

$$\begin{aligned} \sum_{q,\eta} \lambda_q^{(1)}(\eta) \left[\mathcal{W}_q(\mu)\right]_{\tau_l(\mu)} &= -\sum_{q,\eta} \lambda_q(\eta) \left[\mathcal{W}_q^{(1)}(\mu)\right]_{\tau_l(\mu)} \\ -\sum_{\nu} \tilde{C}_\nu^I C_\mu^I \left[H_{eff}^{\nu\mu(1)}\right]_{\tau_l(\mu)} &- \sum_{\nu} \left(\tilde{C}_\nu^{I(1)} C_\mu^I + \tilde{C}_\nu^I C_\mu^{I(1)} \right) \left[H_{eff}^{\nu\mu}\right]_{\tau_l(\mu)} \quad \forall l, \mu \end{aligned} \tag{3.21}$$

In these equations, the quantity within square brackets in the first term on right hand side of Eq (3.21) is first-derivative of SUMRCC Jacobian matrix with respect to perturbation strength parameter g. The subscript $\hat{H} \to \hat{H}^{(1)}$ in $\left[\mathcal{W}_l(\mu)\right]_{\hat{H}\to\hat{H}^{(1)}}$ means that each occurrence of $\hat{H}$ in the bracketed expression is replaced by the property operator $\hat{H}^{(1)}$. These equations are to be solved in the same order they are presented. Eq (3.17) is same as first-order response equation for cluster amplitudes Eq (2.21) derived in second chapter. Next three equations, Eq (3.18)-(3.20) are again same as Eq (2.17)-(2.19) of second chapter for a specific state I. Eq (3.21) is the equation for $\Lambda^{(1)}$ and it depends on all lower-order quantities. This equation has a structure which is similar to the Z-vector or the zeroth-order Lagrange multiplier equations Eq (3.10). The Jacobian entering both these equations is the same. They only difference is in their inhomogeneous part which contains all the lower-order response quantities.

Eq (3.17) and Eq (3.21) reveal another structure similar to that observed by Jorgensen and coworkers[7] in their SRCC gradient studies. Both these equations share the same Jacobian matrix. In SUMRCC, this is purely a result of choice of the functional, namely Eq (3.9). Any other choice of functional such as the one used by Szalay as in Eq (3.11) does not lead to this structure.

III.4.2 Simplified generic expressions up to third-order molecular properties

Energy derivative of n-th order, $E_I^{(n)}$, is just the value of the functional $\mathcal{J}^{(n)}$, denoted by $\mathcal{J}_{opt}^{(n)}$, when stationary values of $\left\{\Theta^{(m)}\ m=0,n\right\}$ are substituted in it. Therefore, $\mathcal{J}_{opt}^{(n)}$ can be considered as the required energy derivative, and E_I can be treated as another Lagrangian multiplier. By using the $(2n+1)$ rule for $C_\mu^{I(n)}$, $\tilde{C}_\mu^{I(n)}$ and $T^{(n)}$, and the $(2n+2)$ rule for Lagrangian multipliers $\Lambda^{(n)}$ and $E_I^{(n)}$, the following quantities are identified to be necessarily absent in final simplified expressions for $\left\{\mathcal{J}_{opt}^{(n)}, n=1,\ldots,3\right\}$.

$$\mathcal{J}_{opt}^{(1)} \Rightarrow \left\{C^{(1)},\tilde{C}^{(1)},T^{(1)},E^{(1)},\Lambda^{(1)}\right\} \tag{3.22.1}$$

$$\mathcal{J}_{opt}^{(2)} \Rightarrow \left\{C^{(2)},\tilde{C}^{(2)},T^{(2)},E^{(2)},E^{(1)},\Lambda^{(2)},\Lambda^{(1)}\right\} \tag{3.22.2}$$

$$\mathcal{J}_{opt}^{(3)} \Rightarrow \left\{C^{(3)},\tilde{C}^{(3)},C^{(2)},\tilde{C}^{(2)},T^{(3)},T^{(2)},E^{(3)},E^{(2)},\Lambda^{(3)},\Lambda^{(2)}\right\} \tag{3.22.3}$$

Simplified generic expression for $\left\{\mathcal{J}_{opt}^{(n)}, n=1,\ldots,3\right\}$ can be obtained by deriving explicit expression for $\left\{\boldsymbol{\mathcal{J}}^{(n)}, n=1,\ldots,3\right\}$ using Taylor series expansion and deleting various quantities $\boldsymbol{\Theta}^{(n)}$ which are not needed according Eq (3.22.1)-(3.22.3). For each response quantity which needs to be eliminated from these expressions, they get eliminated when appropriate lower-order response equations for the conjugate quantity is used. The resulting generic expressions for molecular properties up to third-order molecular properties (dipole moment, polarizability and hyperpolarizabilities) are presented below. In the following, subscript $T^{(n)}$ on a bracketed expression indicates retention of only terms containing $\left\{T^{(m)}, m=0,\ldots,n\right\}$.

$$\mathcal{J}_{opt}^{(1)} = \sum_{\mu\nu} \tilde{C}_{\nu}^{I} C_{\mu}^{I} \left[H_{eff}^{\nu\mu(1)} \right]_{T^{(0)}} + \sum_{q,\eta} \lambda_q(\eta) \left[\mathcal{W}_q^{(1)}(\eta) \right]_{T^{(0)}} \tag{3.23}$$

$$\begin{aligned} \mathcal{J}_{opt}^{(2)} &= \sum_{\mu\nu} \tilde{C}_{\nu}^{I} C_{\mu}^{I} \left[H_{eff}^{\nu\mu(2)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q(\eta) \left[\mathcal{W}_q^{(2)}(\eta) \right]_{T^{(1)}} \\ &-2\left(\sum_{\mu\nu} \tilde{C}_{\nu}^{I(1)} C_{\mu}^{I(1)} H_{eff}^{\nu\mu} - E \sum_{\mu} \tilde{C}_{\mu}^{I(1)} C_{\mu}^{I(1)} \right) \end{aligned} \tag{3.24}$$

$$\begin{aligned} \mathcal{J}_{opt}^{(3)} &= \sum_{\mu\nu} \tilde{C}_{\nu}^{I} C_{\mu}^{I} \left[H_{eff}^{\nu\mu(3)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q(\eta) \left[\mathcal{W}_q^{(3)}(\eta) \right]_{T^{(1)}} \\ &+3 \sum_{q,\eta} \lambda_q^{(1)}(\eta) \left[\mathcal{W}_q^{(2)}(\eta) \right]_{T^{(1)}} \\ &+6\left(\sum_{\mu\nu} \tilde{C}_{\nu}^{I(1)} C_{\mu}^{I(1)} \left[H_{eff}^{\nu\mu(1)} \right]_{T^{(1)}} - E_I^{(1)} \sum_{\mu} \tilde{C}_{\mu}^{I(1)} C_{\mu}^{I(1)} \right) \\ &+3\left(\sum_{\mu\nu} \left(\tilde{C}_{\nu}^{I(1)} C_{\mu}^{I} + \tilde{C}_{\nu}^{I} C_{\mu}^{I(1)} \right) \left[H_{eff}^{\nu\mu(2)} \right]_{T^{(1)}} \right) \end{aligned} \tag{3.25}$$

III.5 Conclusions

Due to its simplicity, CVA has been a successful framework to derive efficient expressions for higher-order properties in SRCC. Automatic inclusion of Z-vector like benefits is also transparent in this approach. In this chapter, we have formulated a CVA functional which encompasses the state-dependent Z-vector method described in the previous chapter. Unlike in SRCC where there is only one functional, in MRCC many equally valid different functionals are possible. Although all these functionals finally yield same results for properties, intermediate results such as Lagrange multipliers will be different. Finally, the results of section III.4 illustrate the advantage of CVA for non-stationary theories over Handy-Schaefer elimination technique. Using this approach, it is particularly easy to derive expressions for higher-order properties and apply $(2n+1)$ and $(2n+2)$ rules to simplify them. Although inclusion of orbital response has not been carried out in this formulation, it can be easily carried out along the lines suggested by Jorgensen and coworkers in SRCC developments.[7]

References

1. S. T. Epstein, *The Variation Principle in Quantum Chemistry*, (Academic, New York, 1974)
2. N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984)
3. E. A. Salter and R. J. Bartlett, J. Chem. Phys. **90**, 1767 (1989)
4. T. Helgaker and P. Jorgensen, Adv. Quant. Chem. **19**, 183 (1988)
5. T. Helgaker and P. Jorgensen, Theor. Chim. Acta. **75**, 111 (1989)
6. P. Jorgensen and T. Helgaker J. Chem. Phys. **89**, 1560 (1988)
7. H. Koch, H. J. A. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria, H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990)
8. H. Koch and P. Jorgensen, J. Chem. Phys. **93**, 3333 (1990)
9. P. G. Szalay, Int. J. Quant. Chem. **55**, 151 (1994)
10. (a) G. Fitzgerald, R. J. Harrison, and R. J. Bartlett, J. Chem. Phys. **85**, 5143 (1986) (b) E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989)

11. (a) S. Pal and K. B. Ghose, Curr. Science. **63**, 667 (1992) (b) S. Pal, Theor. Chim. Acta. **66**, 151 (1984)

Chapter IV

Pilot application of state-universal MRCC theory for the computation of molecular properties

IV.1 Introduction

Molecular property surfaces are obtained by plotting values of a molecular property (such as different components of dipole moment) for a specific electronic state of a molecule at different nuclear geometries, and may be seen as an extension of concept of potential energy surfaces (PES).[1] In so much as PES is useful for defining rovibronic states, for studying nuclear dynamics involving coupling between different electronic states, and for monitoring chemical reaction progress, molecular property surfaces are useful for calculation of quantities such as spectral line intensities and for a qualitative and quantitative understanding of finer spectroscopic effects. For example, various derivatives of dipole moment and dipole polarizability with respect to nuclear perturbations along normal coordinates are important inputs for computing spectral line intensities of infra-red and Raman active vibrational modes. An overview of importance of property surfaces in spectroscopy along with a discussion on issues involved in their ab-initio computation may be found in a series of articles in a monograph edited by Jorgensen and Simons.[2]

Despite their importance, derivation of even simple property surfaces, such as dipole moment or transition moment surfaces, from experimental spectroscopic data is difficult, for various reasons.[3] On the other hand, their ab-initio computation is relatively straightforward, and several examples may be found in the monograph quoted above.

As discussed in the first chapter, molecular properties are calculated using either finite-field or analytic response approach.[1] Finite-field approach involves explicit computation of molecular energy in presence of a small field perturbation of different strengths around the zero-field in different directions. The computed energies are then numerically fitted, usually to a polynomial or a spline, and different derivatives at zero-field strength are evaluated. This approach is very sensitive to accuracy of energy. Due to loss of precision that occurs in this differentiation procedure, usually energy needs to be one or two orders more accurate than the accuracy needed in the property being computed. Furthermore, a large number of energy calculations are needed, especially for higher-order properties and geometric derivatives. On the other hand, second approach involves analytic computation of molecular energy derivatives at zero-field by analytical solution of appropriate response quantities. This approach is not so sensitive to accuracy of energy computation, and properties obtained are about as accurate as energy itself. With analytic response developments for efficient computation of properties, especially for non-variational theories, cost of a first-derivative computation is roughly about the same as a single-point energy computation. For these reasons, analytic approach is usually preferred. A suitable combination of both approaches is also used, especially for higher-order properties where analytic derivatives are not available.[4]

Applications of MRCC theories for computation of molecular properties have been carried out recently by Pal and coworkers.[5-6] Using valence-universal MRCC theory, Pal and coworkers have calculated dipole moments of open shell radicals and excited state dipole moments of several small molecules.[6] A time dependent response approach for valence-universal MRCC has also been formulated by Ajitha and Pal to enable computation of frequency-dependent properties.[7] No applications of state-universal

MRCC theory to compute molecular properties have been reported so far. Being suited to the description of potential energy surfaces,[8] it is expected to be useful for molecular property surfaces.

In this chapter, we report a pilot application of complete model space based SUMRCC theory for computation of dipole moment curves of ground and three low-lying excited states of HF molecule using a double-zeta quality basis set. Towards this end, the SUMRCC theory with singles and doubles (SD) approximation for cluster amplitudes as well as effective Hamiltonian matrix elements has been implemented and validated against previous available results. Both finite-field and analytic approach using the state-dependent Z-vector method described in second chapter, have been employed in property calculations. Attempts to progress to higher basis sets and to other simple hetero-nuclear diatomic molecules are found to result in convergence difficulties due to poorer description of a state. Different approaches available in literature to overcome these convergence problems are discussed.

IV.2 Application of SUMRCC to the dissociation of HF molecule

Several researchers have implemented and applied SUMRCC theory to study potential energy surfaces of small molecular systems. First implementation and applications of non-spin adapted version in spin-orbital basis were reported by Meissner, Jankowski and Wasilewski,[9] who referred it to as multi-reference coupled electron-pair method (MR-CEPM). Cluster operators were approximated by two-body parts (doubles) and non-linear parts were included in direct as well as renormalization terms. Linear version of the method was also discussed. They have applied MR-CEPM to study minimal basis set H_8 model system in which quasi-degeneracy may be continuously varied, as well as to the classic case of C_{2v} insertion of Be into H_2.

An orthogonally spin-adapted version of the theory was derived by Jezioroski and Paldus,[10] within singles and doubles approximation for cluster amplitudes. This applies for two-dimensional complete model spaces spanned by two totally symmetric closed-shell types of determinants differing in two valence orbitals of different spatial symmetry. Paldus and coworkers[11-13] have applied it to study the quasi-degeneracy in H_4 model system. They have studied the performance of different approximations for direct and renormalization terms to describe quasi-degeneracy in such simple model systems, and find that inclusion of up to quadratic terms in renormalization terms leads to results in good agreement with full-CI.[13]

Kucharski and Bartlett[14] have presented complete diagrammatic equations in spin-orbital form using singles and doubles approximation for cluster amplitudes. They developed the standard quadratic approximation in which only linear and quadratic terms are retained in renormalization terms while considering full expansion for the direct term. Bartlett and coworkers have applied it to study model H_4 and H_8 systems[15-16], and ground and three low-lying excited state potential energy surfaces of Li_2.[17] Spin-orbital formulation provides access to open-shell states and this has been advantageously used by Balkova and Bartlett.[18] This formulation has been successfully applied by Bartlett and coworkers[19] to a special model space spanned by two open-shell determinants to study open-shell singlet states of ozone and other small molecules. Incomplete model space version of SUMRCC developed by Meissner and coworkers[20] has also found some applications. Balkova and coworkers[21] have applied this formalism to study ground and several excited states of LiH. Berkovic and Kaldor[22] have also employed it in their studies on excited states of N_2 molecule and vertical excitations in H_2O. Balkova and coworkers[23] have also developed non-iterative inclusion of triples and applied it to study cyclo-butadiene.

Towards our pilot application of state-universal MRCC for molecular properties, we have implemented the theory using spin-orbital formulation of Kucharski and Bartlett.[14] We have used singles and doubles approximation for the cluster amplitudes as well as for the effective Hamiltonian. We have included cubic and quartic terms in renormalization terms. For model spaces containing determinants differing at most by double excitations, this approximation is complete and does not differ significantly from the standard quadratic approximation, and is useful to study dissociation of single bonds. We have validated correctness of our implementation against results of Balkova and coworkers,[17] and by further internal self-consistency checks. The orbitals have been obtained by carrying out SCF calculations on a closed-shell determinant in model space.

We have applied this to study the dissociation of HF molecule using Huzinaga-Hay double-zeta quality basis set.[24] The model space employed was formed by distributing two electrons among highest occupied and lowest unoccupied molecular orbitals of σ symmetry. Within spin-orbital description, this results in a six-dimensional model space. Two determinants in this model space correspond to triplet configurations with $M_S = +1, -1$ and form one-dimensional complete model spaces of their own (the effective Hamiltonian is block-diagonal). The remaining four determinants with $M_S = 0$ form another complete model space. For homo-nuclear diatomic molecules, both these active orbitals belong to different irreducible representations (σ_g and σ_u) of $D_{\infty h}$ symmetry group. Therefore, this four-dimensional model space in this case further splits into two two-dimensional complete model spaces, one with two completely symmetric closed-shell singlet determinants, and other with two open-shell determinants with

$M_S = 0$. Open-shell singlet and triplet states with $M_S = 0$ emerge from the latter model space. In SUMRCC, these states are spin-contaminated. In case of hetero-nuclear diatomic molecules as considered here, both active orbitals belong to same irreducible representation (σ) of $C_{\infty v}$ symmetry group. For this reason, closed-shell and open-shell states are completely coupled, and four-dimensional model space can not be reduced further. In our calculations, we have retained $M_S = +1, -1$ configurations to get an estimate of spin-contamination in $M_S = 0$ triplet state emerging from four-dimensional manifold. Difference in energies of $M_S = +1, -1$ and $M_S = 0$ triplet state is an indication of extent of spin-contamination. We have observed that this difference is about a fraction of a milli-hartrees and hence spin-contamination is expected to be small.

The results of these calculation are presented in Fig.IV.1 where potential energy curves for ground and three low-lying excited states of have been shown along with corresponding Full-CI results. It may be noticed that for the first three states (closed-shell ground state $X^1\Sigma^+$, open-shell triplet state $a^3\Sigma^+$, and open-shell singlet state $A^1\Sigma^+$), the results of SUMRCC differ with Full-CI results only by a few milli-hartrees, with large differences observed at non-degenerate regions. However, for the fourth state (second singlet state $B^1\Sigma^+$) lying higher up in energy, consistent differences of 15-40 milli-hartrees are observed indicating a relatively poor description.

An observation of the contribution of each model space determinants to different states at different geometries reveals some interesting features. Around the non-degenerate region at equilibrium geometry, the ground state $X^1\Sigma^+$, as expected, is dominated by closed-shell model space determinant formed by highest occupied molecular orbitals with small contributions from other three determinants. Open-shell determinants have smaller contributions than the bi-excited closed-shell model space determinant. The $a^3\Sigma^+$ and $A^1\Sigma^+$ states are dominated by open-shell model space determinants with relatively small contributions from the closed-shell model space determinants. The triplet state does not have any detectable contribution from the closed-shell model space determinants at any bond distance. The $B^1\Sigma^+$ state is dominated by bi-excited closed-shell model space determinant. This shows that at equilibrium geometry, singlet states may be approximately divided into closed-shell and open-shell type of states. As the bond is stretched, contributions of open-shell model space determinants in closed-shell singlet states and vice-versa slowly grow, and making a clear distinction is unclear. The nature of these states changes significantly as the molecule dissociates. As seen in Fig.IV.1, the states $A^1\Sigma^+$ and $B^1\Sigma^+$, go through a minima and dissociate into different channels.

IV.3 Dipole moment surfaces of ground and low-lying excited states of HF molecule

Experimental[25] as well as ab-initio computed[3,26] ground state dipole moment curves for HF are available in literature for different ranges of bond distance. It is known that ground state dipole moment function of HF undergoes a maxima at intermediate bond distances.[3,25-26] However, very little is known about behaviour of excited state dipole moment curves. To the best of our knowledge, excited state dipole moment curves are not available.

We have calculated dipole moment curves of ground and three excited states of HF reported in previous section. Both finite-field and analytic calculations have been carried out. For finite-field calculations, constant electric field perturbation along the bond axis has been included at the SCF level, and the relaxed orbitals so obtained have been used for correlated studies. At stretched geometries orbitals change significantly and such orbital relaxation effects can not be easily accounted by singles amplitudes within the cluster operators. At each bond distance, five different field strength values in each direction have been used. Dipole moments have been obtained by fitting the resulting energies to appropriate polynomials.

For analytic calculations, the state-dependent Z-vector method derived in the second chapter has been implemented. For each state, the Z-vector is obtained by solving the Z-vector equations. This is followed by its contraction with appropriate terms involving cluster amplitudes and dipole moment matrix elements in molecular orbital basis to calculate its contribution to electronic part of total dipole moment. Orbital relaxation effects have not been included in these calculations. The Z-vector obtained after first iteration of Z-vector equations has been used for computation of dipole moments.[27]

The results are presented as dipole moment curves in Fig.IV.2-IV.3 and tabulated as numerical values in Table.IV.1-IV.2. Full-CI dipole moments for all three excited states are not available, and in these cases, comparison can be made with corresponding finite-field results. Fig.IV.2 clearly shows that ground state dipole moment function, as expected, goes through a maximum around 1.5R$_e$ (R$_e$=1.7328 atomic units). Again, as expected, as the bond is stretched, dipole moments of both ground state as well as open-shell triplet state vanish indicating homolytic dissociation.

Agreement between different calculations can be better analyzed by looking at Table.IV.1. For the ground state, in the range R$_e$-2R$_e$, finite-field results are in better agreement with full-CI results than their analytic counterparts. The disagreement between analytic and full-CI results may be partly attributed to the use of incompletely converged Z-vector or to the neglect of orbital relaxation effects in analytic calculation. The agreement between finite-field and full-CI results degrades as the bond is stretched. In fact, after $2R_e$, analytic results are in better agreement with full-CI results despite non-inclusion of orbital relaxation effects and the use of incompletely converged Z-vector. For the triplet state, agreement between finite-field and analytic results is poor in the range R_e-$1.5R_e$, and improves at higher values of bond distances. Interestingly, after $2.5R_e$, finite-field results show slight increase in dipole moment and it does not go to zero at the rate it is expected. This is counter intuitive, and we believe that this is an artifact of finite-field calculation. On the other hand, analytic results show the correct trend at large distances.

For two singlet excited states ($A^1\Sigma^+$ and $B^1\Sigma^+$), the results are presented in Fig.IV.3 and Table.IV.2. The dipole moment curves going to infinity clearly indicate that for these states, dissociation leads to ionic fragments (heterolytic dissociation). The first singlet state has dipole moment with same sign as the ground state dipole moment. This means that, for this state, ionic fragments are H^+ and F^-. For the second state, sign of dipole moment is opposite of the first one indicating that corresponding ionic fragments are H^- and F^+. A positive charge on highly electronegative Fluorine atom is consistent with the fact that this state is high up in energy compared to the first one by at least about 0.4 hartrees as can be seen in Fig.IV.1.

IV.4 Use of higher quality basis sets and applications to other hetero-nuclear diatomic molecules

Although the results presented in previous sections show correct trends and are in general agreement with Full-CI results, studies using higher basis sets are necessary to obtain dipole moment surfaces which can be used in quantitative spectroscopic calculations. Towards this end, we have attempted to progress to the next level basis set, namely the double-zeta with polarization function (DZP) basis set. Despite our experimentation with different orbital energy shifting schemes advocated by Balkova and coworkers,[17] the simple Jacobi type iteration procedure used for solving SUMRCC equations does not converge. Initial iterations typically converge to an average of 1.0E-04 for energies before starting to oscillate and finally diverge. This happens at all bond distances within the range considered in the above case. SUMRCC calculations on some other hetero-diatomic molecules, namely LiH and LiF, were also attempted with DZ and DZP basis sets, using the same complete model space. Similar convergence problems have been encountered.

The inclusion of bi-excited configuration within the complete model space appears to be the cause of these convergence difficulties. The observation that this configuration is one among the dominating ones in the poorly described second singlet excited state ($B^1\Sigma^+$) which dissociates into H^- and F^+ fragments is indicative of this. Intuitively, such a state is necessarily high up in energy. For proper description of such a state involving positive charge on Fluorine atom, several other excited configurations involving excitations to different virtual orbitals of σ symmetry are equally important. In DZ basis set, such virtual orbitals are higher in energy compared to the lowest unoccupied orbital, and hence they do not cause convergence difficulties. When higher basis sets such as DZP are considered, such orbitals get stabilized and their energy comes down. Consequently, configurations involving these orbitals also come down in energy, coming closer to energy of the bi-excited configuration included in the model space. These low-lying intruder states affect convergence of SUMRCC calculations with higher basis sets.

Balkova and coworkers[21] have studied dissociation of LiH molecule using incomplete model space version of state-universal MRCC. In their calculations, they do not include corresponding bi-excited configuration within the model space. As a consequence, they do not encounter serious convergence difficulties. Use of such incomplete model spaces to alleviate convergence difficulties of complete model space based MRCC theories is an attractive alternative that has been pursued in literature. Although similar kind of incomplete model space may be envisaged for our higher basis set studies, our SUMRCC program is not equipped to deal with such general incomplete model spaces. Furthermore, as explained in the next chapter, the analytic response approach for incomplete model space based MRCC theories is somewhat different from the complete model space one followed here.

Use of convergence accelerators is another alternative. Commonly used ones in SRCC are orbital energy shifting techniques[17], method of direct inversion in iterative subspace (DIIS)[28] and the closely related reduced linear equation (RLE) method[29]. We have tried energy shifting and RLE method without much success. Our experience shows that these methods can efficiently accelerate convergence in cases where there is a converging trend. However, most often they fail to induce convergence in divergent cases.

Piecuch and Adamowicz[30a] have proposed a quasi-linearization algorithm which seems to be capable of inducing convergence even in divergent cases. Piecuch and coworkers[30b] have successfully applied this method to the orthogonally spin-adapted version of SUMRCC theory. Similar approach may be followed for spin-orbital based formulation to increase its scope and applicability.

IV.5 Conclusions

Our pilot application of state-universal MRCC theory to calculate ground and low-lying excited state dipole moment curves of HF molecule, using both finite-field and analytic approaches, highlights its potential usefulness. Use of higher basis sets, which is essential for production of high quality curves for computation of spectroscopic quantities, has not been possible due to severe convergence difficulties. This is shown to happen due to poor description of a particular high lying state in the manifold. Use of an incomplete model space without the bi-excited configuration, and use of quasi-linearization based convergence accelerators have been suggested as strategies to overcome the convergence difficulties.

We conclude this chapter with a brief discussion on possible future of SUMRCC theory and its applicability. Attractive features of SUMRCC have been (a) Its conceptual simplicity and close similarity with SRCC (b) Size-extensivity (c) Suitability for potential energy surfaces (d) Direct relation to MRCI (e) Obtaining the states without the need to step out of Hilbert space (f) Lesser number of parameters as compared to VUMRCC. However, its weak points have been (i) Difficulty to cast into a general orthogonally spin-adapted formulation (ii) Large number of renormalization terms, especially when Baker-Hausdorf formula is used (iii) Far more severe intruder state problem encountered in potential energy surfaces calculations than in spectroscopic difference calculations.

Despite all its attractive features, applications of SUMRCC have been rather limited. In fact, to the best of our knowledge, no significant applications have been reported since 1995. There appears to be some kind of pessimism over its future. While these weak points still remain to overcome, there have been some more works recently, mainly by Paldus and coworkers[31-33], and Piecuch[34]. Furthermore, Hubac and coworkers[35], and Mahapatra, Mukherjee and coworkers[36] have employed the state-universal Jezioroski-Monkhorst ansatz[8] to formulate their state-selective MRCC theories. Now a days, such theories are considered to be better suited to avoid intruder state problems associated with Hilbert-space type of approaches.

References

1. R. D. Amos, Adv. Chem. Phys, **67**, 99 (1987)
2. P. Jorgensen and J. Simons, *Geometrical Derivatives of Energy Surface and Molecular Properties*, (Reidel, Dordrecht,1986)
3. P. Rosmus and H. J. Werner, in the monograph cited in Ref.1
4. J. F. Gaw and N. C. Handy, in the monograph cited in Ref.1
5. (a) S. Pal, Phys. Rev. **A39**, 39 (1989) (b) S. Pal, Int. J. Quant. Chem. **41**, 443 (1992)
6. (a) D. Ajitha, N. Vaval, and S. Pal, J. Chem. Phys. **110**, 2316 (1999) (b) D. Ajitha and S. Pal, Chem. Phys. Lett. **309**, 457 (1999) (c) D. Ajitha and S. Pal , J. Chem. Phys. **114**, 3380 (2001) (d) N. Vaval and S. Pal, Chem. Phys. Lett. **300**, 125 (1999)
7. D. Ajitha and S. Pal, Phys. Rev. **A56**, 2658 (1997)
8. B. Jezioroski and H. J. Monkhorst, Phys. Rev. **A24**, 1668 (1982)
9. L. Meissner, K. Jankowski and J. Wasilewski, Int. J. Quant. Chem. **34**, 535 (1888)
10. B. Jezioroski and J. Paldus, J. Chem. Phys. **88**, 5673 (1988)
11. J. Paldus, L. Pylypow and B. Jezioroski, in *Many-body methods in Quantum Chemistry, Lecture notes in Chemistry,* edited by U. Kaldor (Springer-Verlag, 1989) Vol.**52**, p151
12. J. Paldus, P. Piecuch, B. Jezioroski, and L. Pylypow, in *Recent Advances in Many-Body Theories*, edited by T. L. Ainsworthy, C. E. Campbell, B. E. Clements, and E. Krotschek (Plenum, New York, 1992), Vol.**3**, p287
13. J. Paldus, P. Piecuch, L. Polypow, and B. Jezioroski, Phys. Rev. **A47**, 2738 (1993) (b) P. Piecuch and J. Paldus, Phys. Rev. **A49**, 3479 (1994) (c) P. Piecuch and J. Paldus, Theor. Chim. Acta. **83**, 69 (1992) (c) P. Piecuch and J. Paldus, J. Chem. Phys. **101**, 5875 (1994)

14. S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. 95, 8227 (1991)
15. A. Balkova, S. A. Kucharski, L. Meissner, and R. J. Bartlett, Theor. Chim. Acta. **80**, 335 (1991)
16. S. A. Kucharski, A. Balkova, P.G. Szalay, and R. J. Bartlett, J. Chem. Phys. **97**, 4289 (1992)
17. A. Balkova, S. A. Kucharski, and R. J. Bartlett, Chem. Phys. Lett. **182**, 511 (1991)
18. A. Balkova and R. J. Bartlett, Chem. Phys. Lett. **193**, 364 (1992)
19. (a) A. Balkova and R. J. Bartlett, J. Chem. Phys. **99**, 7907 (1993) (b) P. G. Szalay and R. J. Bartlett, J. Chem. Phys. **101**, 4936 (1994) (c) A. Balkova and R. J. Bartlett, J. Chem. Phys. **102**, 7116 (1995)
20. (a) L. Meissner, S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **91**, 6187 (1989) (b) L. Meissner and R. J. Bartlett, J. Chem. Phys. **92**, 561 (1990)
21. A. Balkova, S. A. Kucharski, L. Meissner, and R. J. Bartlett, J. Chem. Phys. **95**, 4311 (1991)
22. (a) S. Berkovic and U. Kaldor, Chem. Phys. Lett. **199**, 42 (1992) (b) S. Berkovic and U. Kaldor, J. Chem. Phys. **98**, 3090 (1993)
23. A. Balkova and R. J. Bartlett, J. Chem. Phys. **101**, 8972 (1994)
24. T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III, (Plenum, New York, 1976) p1
25. (a) F. H de Leeuw and A. Dymanus, J. Mol. Spectroscopy **48**, 427 (1973) (b) R. N. Sileo and T. A. Cool, J. Chem. Phys. **65**, 117 (1976)
26. (a) G. C. Lie, J. Chem. Phys. **60**, 2991 (1973) (b) H. J. Werner and P. Rosmus, J. Chem. Phys. **73**, 2319 (1980)

27. The results presented here are correct up to first iteration of Z-vector equations. The iterative procedure for solution of Z-vector equations shows an initial converging trend. However, after a few iterations, oscillations and slow divergence set in. The causes for this behaviour are currently being investigated. Although the Z-vectors obtained at subsequent iterations before the divergence sets in have been observed to yield better results as compared to the first iteration, we have chosen to include only the first iteration results for the sake of uniformity.
28. G. E. Scuseria, T. J. Lee and H. F. Schaefer, Chem. Phys. Lett. **130**, 236 (1986)
29. G. D. Purvis III and R. J. Bartlett. J. Chem. Phys. **75**, 1284 (1981)
30. (a) P. Piecuch and L. Adamowicz, J. Chem. Phys. **100**, 5857 (1994) (b) P. Piecuch and J. I. Landman, Parallel Computing **26**, 913 (2000)
31. J. Paldus and X. Li, J. Chem. Phys. **118**, 6769 (2003)
32. (a) X. Li and J. Paldus. J. Chem. Phys. **119**, 5320 (2003) (b) ibid. **119**, 5334 (2003) (c) ibid. **119**, 5346 (2003) (d) ibid. **120**, 5890 (2004)
34. J. Paldus and X. Li. Coll. Czech. Chem. Comm. **69**, 90 (2004)
35. P. Piecuch and K. Kowalski, Int. J. Mol. Sci. **3**, 676 (2002)
36. J. Masik and I. Hubac, Adv. Quant. Chem. **31**, 75 (1999)
37. U. S. Mahapatra, B. Datta, B. Bandopadhyay and D. Mukherjee, Adv. Quant. Chem. **30**, 163 (1998)

Fig.IV.1 Ponteial energy curves of ground and three low-lying excited states of HF molecule

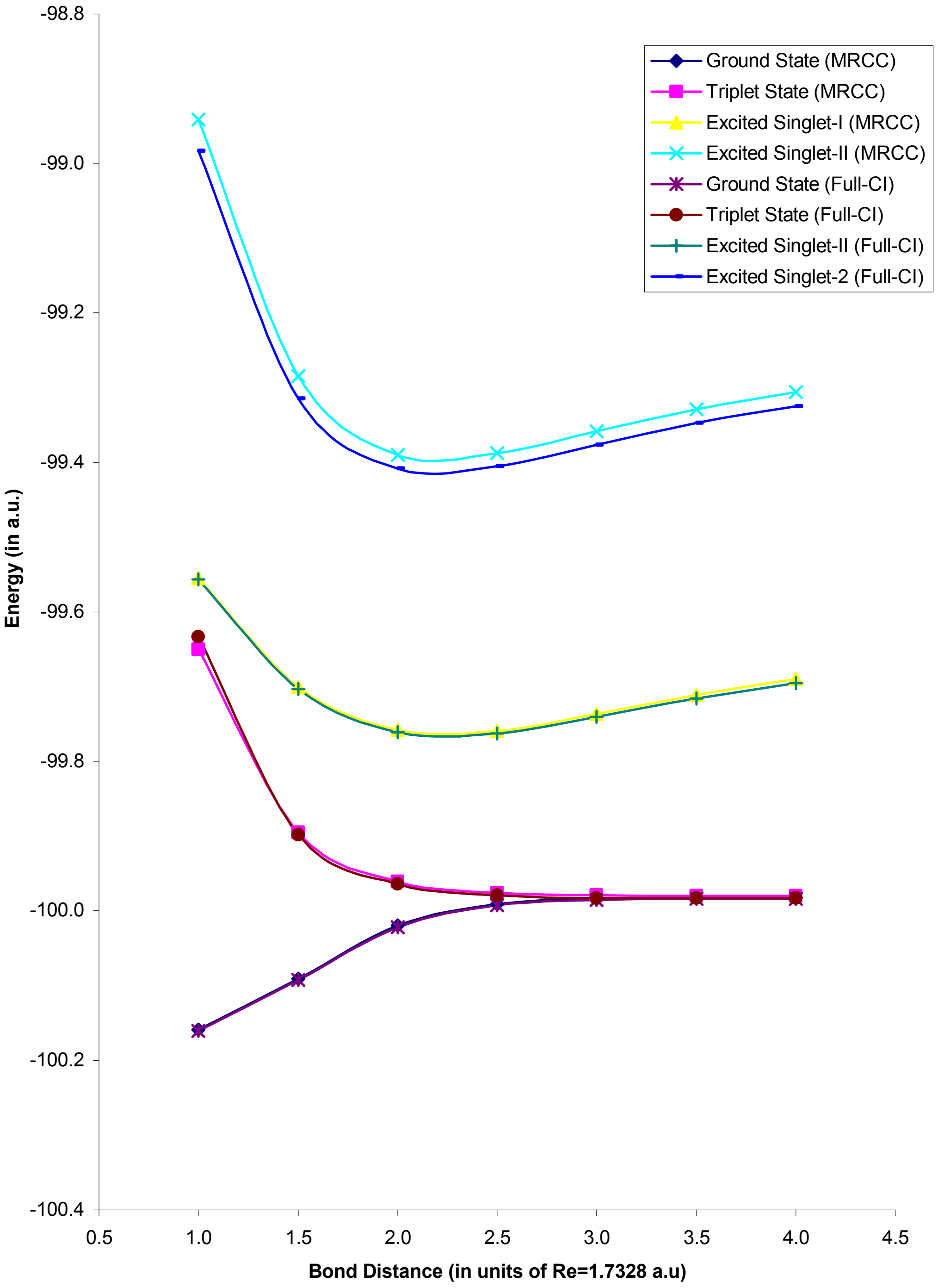

Fig.IV.2 : Dipole moment curves for ground state and triplet states of HF

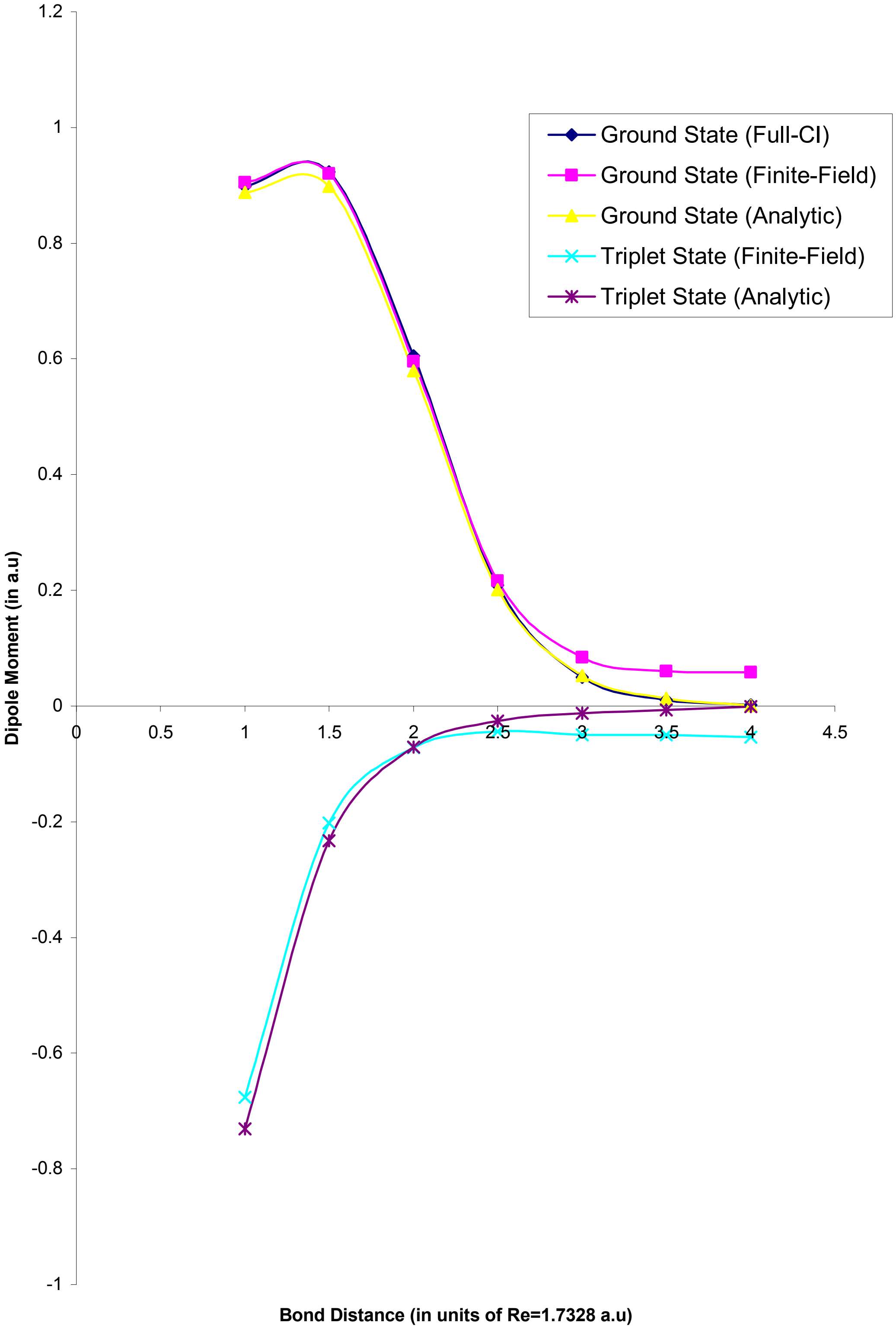

Fig.IV.3 : Dipole moment curves for two excited singlet states of HF

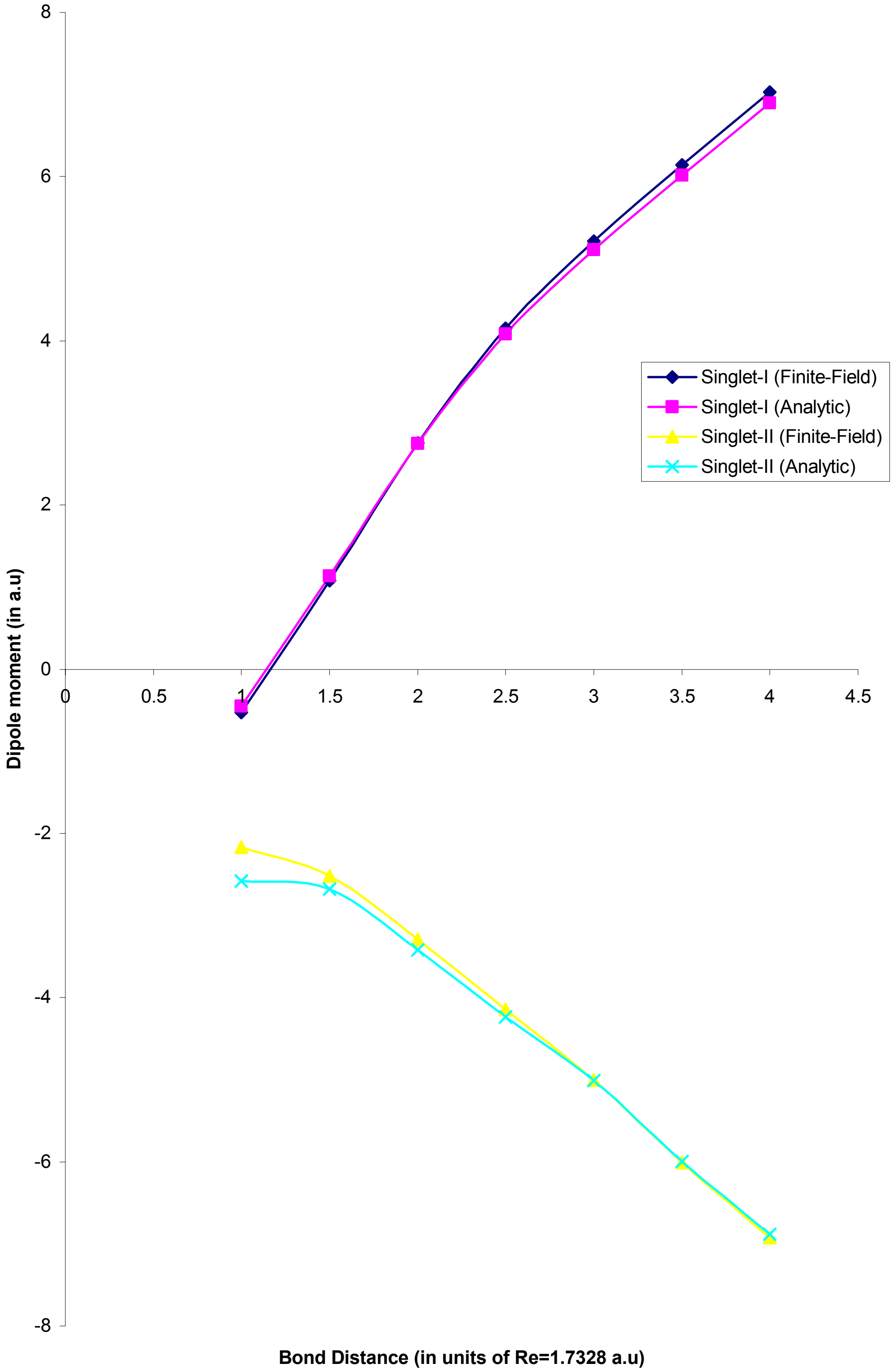

Table IV.1 : Dipole moments (in atomic units) of ground state ($X^1\Sigma^+$) and triplet state ($a^3\Sigma^+$) at different values of Bond distance (in units of R$_e$ = 1.7328 atomic units). Positive values of dipole moment refer to negative charge on Fluorine.

Bond distance	Ground State ($X^1\Sigma^+$)			Triplet State ($a^3\Sigma^+$)	
	Full-CI	SUMRCC Finite Field	SUMRCC Analytic Z-vector	SUMRCC Finite Field	SUMRCC Analytic Z-vector
1.0	0.898	0.905	0.888	-0.676	-0.731
1.5	0.923	0.920	0.898	-0.202	-0.233
2.0	0.605	0.596	0.579	-0.072	-0.071
2.5	0.209	0.216	0.201	-0.044	-0.026
3.0	0.050	0.084	0.053	-0.050	-0.013
3.5	0.010	0.060	0.013	-0.050	-0.007
4.0	0.002	0.058	0.001	-0.054	-0.001

Table IV.2 : Dipole moments (in atomic units) of two singlet states ($A^1\Sigma^+$ and $B^1\Sigma^+$) at different values of Bond distance (in units of R$_e$ = 1.7328 atomic units). Positive values of dipole moment refer to negative charge on Fluorine.

Bond distance	Dipole Moment of First Singlet State $A^1\Sigma^+$		Dipole Moment of Second Singlet State $B^1\Sigma^+$	
	SUMRCC Finite Field	SUMRCC Analytic Z-vector	SUMRCC Finite Field	SUMRCC Analytic Z-vector
1.0	-0.530	-0.449	-2.168	-2.578
1.5	1.082	1.136	-2.517	-2.677
2.0	2.756	2.750	-3.296	-3.420
2.5	4.150	4.084	-4.146	-4.233
3.0	5.213	5.112	-5.007	-5.013
3.5	6.139	6.019	-6.010	-5.997
4.0	7.026	6.894	-6.923	-6.881

Chapter V

Constrained variation approach for incomplete model space based state-universal and valence-universal MRCC theories, and its application to higher-order energy response properties using valence-universal MRCC theory

V.1 Introduction

It has been well-documented in literature that complete model space (CMS) based MRCC theories often face convergence difficulties. This has been also noticed in our applications of SUMRCC to simple diatomic molecules, and known remedies have pointed out in the previous chapter. As discussed there, convergence difficulties can, in some cases, be overcome by using different algorithms for the solution of non-linear MRCC equations. However, the very existence of such difficulties can be often traced to failure to meet physical and mathematical requirements of a theory sufficiently. In case of effective Hamiltonian MRCC theories using CMS, this is referred to as the intruder state problem.[1-3] The effective Hamiltonian theory aims at a well-balanced simultaneous description of a manifold of strongly interacting states. A zeroth-order approximation to this manifold is provided by the chosen model space. It is further assumed that this model space is energetically well-separated from its orthogonal complement and weakly interacts with it. This means that determinants from orthogonal complement are not dominant in any of the targeted states.

In practical quasi-degenerate situations involving bond-breaking or excited states, these requirements are not sufficiently met. The necessity of using CMS forces inclusion of certain determinants which are not dominant components of any of required target states, and hence are not really required for their description. As a result, the target manifold is enlarged to include states having no dominant components within the model space. The description of such states becomes poor. Such poorly described states forcefully included in target manifold, by coupling to other states through diagonalisation worsen their description and eventually cause convergence problems. Such states are referred to as intruder states.[1-3]

Different methods have been proposed to overcome the problem of intruder states. Among them, use of incomplete model spaces (IMS) first suggested by Hose and Kaldor[4] seems to be the natural one. Here, only the determinants that are essential for description of the targeted states are included within the model space. However, the crucial concept of effective Hamiltonian is retained. Although IMS had been advocated and used much earlier,[4-8] their use was limited due to size-extensivity issues associated with them. Later on, Mukherjee[9-11] successfully resolved these issues leading to the emergence of fully size-extensive MRCC theories based on IMS.[12-16] Following these developments, IMS have been used in applications of both state-universal[17-18] and valence-universal[19-23] MRCC theories.

Although applications of SUMRCC have been somewhat limited, VUMRCC has been successfully applied for spectroscopic difference energies[19-23], specially for ionization potential (IP), electron affinity (EA) and excitation energies (EE). Therefore, analytic response approach to VUMRCC can be exploited to obtain molecular properties of such ionized and excited states. The ionized states can be obtained using one-valence model spaces of Fock-space. They are denoted by [0,1] and [1,0] for the case of one valence-hole and one valence-particle respectively. These model space form a CMS. On the other hand, the low-lying excited states in most cases can be described approximately using the [1,1] model space of Fock-space.[6-7,9,15,20] This model space consists of determinants with one pair of valence-hole and particle. This model space turns out to be an IMS. Model spaces from higher valence sectors of Fock-space are also in general IMS.[7] The VUMRCC has many applications, but most of them make use of IMS. Hence, it is important that any analytic response approach for MRCC theories must be applicable for IMS as well. The first-order energy response for VUMRCC earlier followed by Pal and coworkers[24-25] did not include the Z-vector method. Therefore, constrained variation approach (CVA) can be used to obtain a formulation for efficient computation of energy response quantities for both CMS and IMS based VUMRCC theories.

In this chapter, the CVA is suitably generalized to general IMS based state-universal and valence-universal MRCC theories. After presenting a brief description of these IMS based MRCC theories, appropriate constrained variation functionals for these theories are formulated. The resulting equations for Lagrange multipliers are analyzed to clarify their structure. For CMS and some special classes of IMS, the present formulation reduces to the one presented in third chapter and to the one proposed by Szalay.[26] The resulting formulation is then applied to generate explicit generic expressions for up to third-order response properties using [0,1], [1,0] and [1,1] Fock-space sector model spaces. Specific diagrammatic expressions for zeroth-order Lagrange multiplier equations for [0,1], [1,0] and [1,1] Fock-space sectors are also presented.

V.2 MRCC theories based on general incomplete model spaces

Use of IMS in effective Hamiltonian theories was first advocated by Hose and Kaldor[4] in their multi-reference MBPT studies. Jezioroski and Monkhorst[5], in their state-universal MRCC formulation, also considered their use. Brandow[6], Lindgren,[7] Haque and Mukherjee[8] and have also used IMS in their valence-universal formulations. However, due to size-extensivity difficulties associated with them, their use was limited and even theoretically unjustified. As mentioned earlier, later on, working on VUMRCC theories based on IMS, Mukherjee[9-11] traced this size-extensivity and associated difficulties to the use of simple intermediate normalization condition. Upon rectification, this quickly led to size-extensive formulations of MRCC theories based on general IMS.[12-16] In this section, we provide a brief description of IMS based formulations highlighting essential differences with corresponding CMS based formulations.

An IMS is generated from a corresponding CMS by excluding some of the determinants not needed for description of desired states. In a CMS, set of excitation operators can be uniquely classified as either closed (internal) or as open (external). While action of a closed operator on a model space determinant generates another model space determinant, action of an open operator on a model space determinant generates a determinant from the complementary space. It can be easily shown that closed operators carry all valence (active) orbital labels and open operators contain at least one non-valence (passive) orbital label. In other words, in a CMS based formulation, classification of excitation operators into closed or open can be done by an inspection of their orbital labels alone. In contrast, this is not possible in IMS based formulations,[12] and in addition to considering their orbital labels, their action on all model space determinants also needs to be considered to decide whether an excitation operator is a closed or an open operator.

In CMS based MRCC formulations, exponential parameterization of wave-operator Ω is easily achieved by expressing it in terms of all open operators. In case of CMS, since product of open operators always gives open operator, such a parameterization naturally leads to implicit intermediate normalization condition $P\Omega P = P$ on Ω. As discussed in the first chapter, this choice of normalization in Bloch equation based approaches leads to effective Hamiltonian H_{eff} being explicitly defined in terms of wave-operator Ω. This leads to easy proof of size-extensivity of the resulting MRCC theories.

As shown by Mukherjee,[9-11] IMS based MRCC theories can not employ intermediate normalization without destroying size-extensivity of the resulting theory. This leads to two important consequences. Firstly, certain excitation operators carrying only valence labels are to be necessarily introduced into parameterization of wave-operator, leading to the loss of intermediate normalization, .i.e. $P\Omega P \neq P$. Secondly, in Bloch equation based approaches, due to absence of intermediate normalization, H_{eff} can not be explicitly defined in terms of wave-operator. As a consequence, it has to be treated as another independent parameter to be solved simultaneously along with wave-operator.[3]

Another essential difference between CMS and IMS based MRCC theories lies in the choice of excitation operators used for generating wave-operator and effective Hamiltonian. In CMS based MRCC theories, only excitation operators with at least one non-valence label are used for defining wave-operator and those with all valence labels are used to define effective Hamiltonian.[3] In other words, the set of excitation operators generating wave-operator is distinct from the set of operators generating effective Hamiltonian. In IMS based MRCC theories, wave-operator, in addition, necessarily includes some excitation operators with all valence labels.[3,9-10,12] This leads to certain degree of freedom[12] in choosing the all valence label operators which need to be included in wave-operator. As a result, different parameterizations, equivalent to choosing different normalizations for wave-operator, are possible. Since some of the all valence label operators may connect two different model space determinants, they also serve to define a corresponding effective Hamiltonian element. This means that the set of excitation operators which generate wave-operator overlaps with the set of excitation operators which generates effective Hamiltonian.[12]

Suitable exponential parameterizations of wave-operator, which includes only those all valence label excitation operators that are really necessary for size-extensivity, have been introduced by Mukherjee[10] for the valence-universal case, and Meissner and coworkers for the state-universal case.[16] Such schemes are convenient, in the sense that, they lead to as many defining equations as the total number of quantities to be determined (Ω and H_{eff}). In the following subsections, we briefly discuss resulting IMS based state-universal and valence-universal MRCC formulations.

V.2.1 State-universal MRCC theory based on general IMS

Consider a general incomplete model space $P = \left\{ \Phi_\mu, \mu = 1, M \right\}$ with dimension M and complementary space Q. The state-universal ansatz of Jezioroski and Monkhorst[5] for the wave-operator can be written as,

$$\Omega = \sum_\mu e^{T_\mu} \,|\, \Phi_\mu \rangle\langle \Phi_\mu \,| \tag{5.1}$$

The structure of cluster operators T_μ in terms of excitation operators with respect to vacuum Φ_μ is same as in CMS formulation, except that, now it includes certain excitation operators carrying only valence labels. Such excitation operators, acting on Φ_μ may generate a determinant from Q space or another model space determinant. Using this ansatz in generalized Bloch-Lindgren equation followed by pre-multiplication with e^{-T_μ} and projection onto P and Q leads to,

$$\langle \chi_l(\mu) \,|\, e^{-T_\mu} \hat{H} e^{T_\mu} \,|\, \Phi_\mu \rangle = \sum_\eta \langle \chi_l(\mu) \,|\, e^{-T_\mu} e^{T_\eta} \,|\, \Phi_\eta \rangle H_{eff}^{\eta\mu} \quad \forall \Phi_\mu, \chi_l \tag{5.2}$$

$$\langle \Phi_\nu | e^{-T_\mu} \hat{H} e^{T_\mu} | \Phi_\mu \rangle = \sum_\eta \langle \Phi_\nu | e^{-T_\mu} e^{T_\eta} | \Phi_\eta \rangle H_{eff}^{\eta\mu} \quad \forall \Phi_\mu, \Phi_\nu \tag{5.3}$$

Eq (5.2) can be used to define cluster amplitudes associated with excitation operators connecting Φ_μ and $\chi_l(\mu)$. However, Eq (5.3) must be used define effective Hamiltonian elements as well as cluster amplitudes associated with excitation operators carrying all valence labels, connecting two model space determinants.

For cluster amplitudes and effective Hamiltonian to be well-defined without introducing any auxiliary conditions, it is necessary to have just as many all-valence-labeled cluster amplitudes and effective Hamiltonian matrix elements as the total number of equations in Eq (5.3). To order to ensure this, for each vacuum Φ_μ, only those all valence excitation operators which are really necessary for connectivity of resulting equations are introduced into corresponding cluster operator T_μ. Such an excitation operator is easily identified by the prescription given by Meissner and coworkers.[16] While acting on Φ_μ, it leads to another model space determinant Φ_ρ. If the same operator, acting on another model space determinant Φ_η, leads to a determinant from complementary space, then such excitation needs to be included in cluster operator T_μ. The corresponding effective Hamiltonian matrix element $H_{eff}^{\rho\mu}$, also connecting Φ_μ and Φ_ρ is explicitly set to zero. As pointed out by Meissner,[16] this is a way to classify excitation operators into those generated by cluster operator and those generated by effective Hamiltonian. Furthermore, this procedure leads to having same number of equations as the number of unknown variables.

It is important to note that Eq (5.3), in general, does not explicitly define effective Hamiltonian in terms of cluster operators. It can be manipulated into the following form.

$$\begin{aligned} H_{eff}^{\nu\mu} &= \langle \Phi_\nu \,|\, e^{-T_\mu} \hat{H} e^{T_\mu} \,|\, \Phi_\mu \rangle \\ &- \sum_{\eta \neq \mu} \langle \Phi_\nu \,|\, \left(e^{-T_\mu} e^{T_\eta} - 1 \right) |\, \Phi_\eta \rangle H_{eff}^{\eta\mu} \quad \forall \Phi_\mu, \Phi_\nu \end{aligned} \tag{5.4}$$

The above expression clearly shows that in IMS based MRCC theories, effective Hamiltonian is recursively defined. For CMS and some special classes of model spaces identified by Meissner,[16a] second term in Eq (5.4) disappears leading to explicit definition of effective Hamiltonian in terms of cluster amplitudes.

V.2.2 Valence-universal MRCC theory based on general IMS

In this subsection, for simplicity, the IMS based valence-universal MRCC formulation of Mukherjee[10] making use of only valence-particles is considered. However, the results are applicable to any IMS containing both valence holes and valence particles.

Consider an IMS $P^{[n]}$, formed by linear span of determinants $\left\{ \Phi_\mu^{[n]} \ \ \forall \mu = 1, \ldots, \dim(P^{[n]}) \right\}$ from n-valence sector. From this parent model space, model spaces $\left\{ P^{[i]}, i = (n-1), \ldots, 0 \right\}$ each containing determinants $\left\{ \Phi_\mu^{[i]} \ \ \forall \mu = 1, \ldots, \dim(P^{[i]}) \right\}$ for lower i-valence sectors are obtained by subduction process, as outlined by Mukherjee.[10] To obtain cluster operators required correlating all these spaces, cluster operators inducing $P^{[n]}$ to $Q^{[n]}$ transitions are considered. All lower i-valence cluster operators are generated by carrying out subduction process on these n-valence cluster operators. Since n-valence operators contain exactly n valence annihilation operators, each of them act on exactly one determinant within $P^{[n]}$. Hence, for each $\Phi_\mu^{[n]}$ in $P^{[n]}$ and a determinant $\chi_l^{[n]}$ in $Q^{[n]}$, exactly one operator needs to be introduced into i-valence cluster operator $T^{[n]}$. Thus, there are no closed n-valence operators in T by choice. However, lower valence cluster operators $T^{[i]}$ will necessarily contain some i-valence closed operators. As shown by Mukherjee,[10] the closed operators for each lower valence sectors which need to go into corresponding valence cluster operator to achieve size-extensivity are automatically generated by subduction process applied to $T^{[n]}$. This leads to following normal-ordered exponential ansatz of Lindgren[7] for wave-operator Ω.[3,7]

$$\Omega = \left\{ e^{T} \right\} \tag{5.5}$$

$$T = \sum_{i=0}^{n} T^{[i]} \tag{5.6}$$

Use of above ansatz in generalized Bloch-Lindgren equation followed by further manipulations lead to separate equations to define i-valence components of Ω and H_{eff}.

$$\left(\overline{H\Omega} - \overline{\Omega H}_{eff} \right)^{[i]} P^{[i]} = 0 \quad \forall i = 0, \ldots, n \tag{5.7}$$

Here, over line represents connected terms. Because of normal-ordered ansatz for Ω, the above equations are partially decoupled, a condition referred to as subsystem embedding condition (SEC).[27] The equations for i-valence sector depends on all lower valence sectors, and hence above equations are solved starting from zero-valence sector. While solving for a specific valence sector, cluster amplitudes and effective Hamiltonian corresponding to lower valence sector are kept frozen. Solving above equations for i-valence sector defines $T^{[i]}$ and $H_{eff}^{[i]}$ in terms of lower valence counterparts. Solutions for a specific i-valence sector are obtained by left projecting of Eq (5.7) with $P^{[n]}$ and $Q^{[n]}$.

$$\langle \chi_l^{[i]} | \left(\overline{H\Omega} - \overline{\Omega H}_{eff} \right)^{[i]} | \Phi_\mu^{[i]} \rangle = 0 \quad \forall \Phi_\mu^{[i]}, \chi_l^{[i]} \tag{5.8}$$

$$\langle \Phi_\nu^{[i]} | \left(\overline{H\Omega} - \overline{\Omega H}_{eff} \right)^{[i]} | \Phi_\mu^{[i]} \rangle = 0 \quad \forall \Phi_\mu^{[i]}, \Phi_\nu^{[i]} \tag{5.9}$$

While Eq (5.8) is used to determine cluster amplitudes associated with open i-valence open operators in $T^{[i]}$, Eq (5.9) determines both closed i-valence cluster amplitudes as well as $H_{eff}^{[i]}$. For highest sector $P^{[n]}$, there are no closed operators in $T^{[n]}$ and hence Eq (5.9) defines only $H_{eff}^{[n]}$. For lower valence sectors, the number of equations in Eq (5.9) is less than the number of unknowns to be determined. As mentioned earlier, this redundancy is eliminated by equating to zero, the elements of $H_{eff}^{[i]}$ connecting a pair of determinants in $P^{[i]}$ which are also connected by a closed i-valence cluster operator in $T^{[i]}$. As pointed out by Mukherjee,[10] this indeed makes the total number of non-zero $H_{eff}^{[i]}$ and closed i-valence cluster amplitudes in $T^{[i]}$ to be the same as the number of equations in Eq (5.9).

For CMS based MRCC theories, Eq (5.9) contains only $H_{eff}^{[i]}$ due to intermediate normalization, and hence, it explicitly defines $H_{eff}^{[i]}$ in terms of $\left\{T^{[m]}, m = 0, i\right\}$. Eq (5.8), in general, also contains lower valence H_{eff} which are also explicitly defined. Hence, for any given valence level, Eq (5.9) for all lower valence expressions can be substituted into Eq (5.8) to eliminate H_{eff}. However, for IMS based MRCC theories, this is no longer possible and H_{eff} can not be explicitly defined in terms of cluster amplitudes.[3,10] Instead, as mentioned earlier, it has to be treated as an independent parameter and should be solved along with cluster amplitudes. Furthermore, in principle, the entire lower valence H_{eff} could appear in Eq (5.8).

V.3 Constrained variation approach for IMS based MRCC theories

A closer look at the structure of equations for general IMS based MRCC theories, both state-universal as well as valence-universal ones, reveals that Handy-Schaefer elimination technique to extend Z-vector method is not feasible. This can be easily attributed to the fact that effective Hamiltonian is not explicitly defined in terms of cluster operator. Hence, first-order energy response, written in terms of first-order effective Hamiltonian response using first-order coupled-perturbed equation, can not be directly written in terms of first-order cluster amplitude response. This makes it difficult to introduce an elimination mechanism to algebraically define a corresponding Z-vector.

On the other hand, a constrained variational approach[28] is definitely feasible. In the following subsections, we construct constrained variation functionals for general IMS based state-universal and valence-universal MRCC theories. The procedure to obtain equations for Lagrange multipliers is also suitably generalized. Some new elements appearing in this generalization are pointed out. For some special classes of IMS, some simplifications are possible in the form of the functional as well as in procedure to obtain Lagrange multipliers.

V.3.1 Constrained variation approach for IMS based state-universal MRCC theory

In the third chapter, constrained variation functional for CMS based state-universal MRCC theory was constructed by associating a Lagrange multiplier with each independent cluster-amplitude. Similarly, here, for each open as well as closed cluster-amplitude, a corresponding Lagrangian multiplier is introduced. In addition, a Lagrangian multiplier for each non-zero effective Hamiltonian element also needs to be introduced. This accounts for the fact that effective Hamiltonian is now not a derived quantity as earlier, but rather an independent quantity having same status as cluster-amplitudes. Denoting Eq (5.2) by $\mathcal{W}_l(\mu)=0$, and Eq (5.3) by $\mathcal{W}_\nu(\mu)=0$, we construct the following functional.

$$\begin{aligned}\mathcal{J}(\Theta) = {} & \sum_{\mu,\nu} \tilde{C}_{I\nu} H_{eff}^{\nu\mu} C_{\mu I} + \sum_{l,\mu} \lambda_l(\mu) \mathcal{W}_l(\mu) + \\ & \sum_{\nu,\mu} \lambda_\nu(\mu) \mathcal{W}_\nu(\mu) - E_I \left(\sum_{\mu} \tilde{C}_{I\mu} C_{\mu I} - 1 \right)\end{aligned} \tag{5.10}$$

$$\Theta = \left\{ T, H_{eff}, \Lambda, \tilde{C}, C, E_I \right\}, \tag{5.11}$$

Open Lagrange multipliers $\lambda_l(\mu)$ correspond to open cluster-amplitudes $t_l(\mu)$. Closed Lagrange multipliers $\lambda_v(\mu)$ correspond to a closed cluster-amplitude in T_μ if such amplitude has been introduced for size-extensivity reasons. Otherwise, they correspond to an effective Hamiltonian matrix element $H_{eff}^{\nu\mu}$. It should be noticed that variable Θ, unlike in CMS based approaches, now includes H_{eff} as well. Introducing a de-excitation operator Λ_μ which contains both these Lagrange multipliers as its amplitudes, we may explicitly rewrite the functional as follows.

$$\begin{aligned}\mathcal{J}(\Theta) = {} & \sum_{\mu,\nu} \tilde{C}_{I\nu} H_{eff}^{\nu\mu} C_{\mu I} + \sum_{\mu} \langle \Phi_\mu | \Lambda_\mu e^{-T_\mu} \hat{H} e^{T_\mu} | \Phi_\mu \rangle \\ & - \sum_{\mu,\nu} \langle \Phi_\mu | \Lambda_\mu e^{-T_\mu} e^{T_\nu} | \Phi_\nu \rangle H_{eff}^{\nu\mu} - E_I \left(\sum_{\mu} \tilde{C}_{I\mu} C_{\mu I} - 1 \right)\end{aligned} \tag{5.12}$$

The procedure to obtain equations for Lagrange multipliers also needs to be generalized. In addition to making the above functional stationary with respect variations in cluster-amplitudes, it has to be made stationary with respect to variations in non-zero effective Hamiltonian matrix elements as well. For variations with respect to effective Hamiltonian and cluster amplitudes, the usual stationarity condition leads to following equations for Lagrange multipliers.

$$\langle \Phi_\mu | \Lambda_\mu e^{-T_\mu} e^{T_\nu} | \Phi_\nu \rangle = \tilde{C}_{I\nu} C_{\mu I} \tag{5.13}$$

$$\begin{aligned}\langle \Phi_\mu | \Lambda_\mu e^{-T_\mu} [\hat{H}, \tau(\mu)] e^{T_\mu} | \Phi_\mu \rangle = {} & \sum_{\nu} \langle \Phi_\nu | \Lambda_\nu e^{-T_\nu} \tau(\mu) e^{T_\mu} | \Phi_\mu \rangle H_{eff}^{\mu\nu} \\ & - \sum_{\nu} \langle \Phi_\mu | \Lambda_\mu e^{-T_\mu} \tau(\mu) e^{T_\nu} | \Phi_\nu \rangle H_{eff}^{\nu\mu}\end{aligned} \tag{5.14}$$

These are linear inhomogeneous equations in Lagrange multipliers Λ_μ. While, Eq (5.13) defines Lagrange multipliers $\lambda_v(\mu)$ which corresponds to a non-zero effective Hamiltonian element $H_{eff}^{v\mu}$, Eq (5.14) defines Lagrange multipliers $\lambda_l(\mu)$ which correspond to cluster-amplitudes associated with open excitation operators $\tau_l(\mu)$ in T_μ as well as Lagrange multipliers $\lambda_v(\mu)$ which correspond to cluster-amplitudes associated with closed excitation operators $\tau_v(\mu)$ included in T_μ. It is interesting to note that only Eq (5.13) contains a non-zero inhomogeneous part. Furthermore, in Eq (5.13), only Lagrange multipliers corresponding to a single vacuum in Φ_μ are present. This equation couples closed and open Lagrange multipliers of a given vacuum. It is in Eq (5.14) where Lagrange multipliers corresponding to different vacuums become coupled. The state-dependency enters through non-zero inhomogeneous term in Eq (5.13).

V.3.2 Constrained variation approach for valence-universal MRCC

Constrained variation approach for valence-universal case closely follows the state-universal case. The main results, i.e., the presence of Lagrange multipliers corresponding to cluster-amplitudes and effective Hamiltonian matrix elements, and modification of variation procedure to consider variations with respect to effective Hamiltonian elements holds true in this case as well. However, an additional new element emerges in this case.

Construction of constrained variational functional for valence-universal MRCC proceeds can be done by introducing a de-excitation operator $\Lambda^{[i]}$ for each i-valence sector. The de-excitation amplitudes in $\Lambda^{[i]}$ are the Lagrange multipliers corresponding to Eq (5.8)-(5.9). Operator $\Lambda^{[i]}$ contains open i-valence operators inducing transitions from $Q^{[i]}$ to $P^{[i]}$-excitations. In addition, it also contains all closed i-valence operators inducing transitions within $P^{[i]}$. As in previous subsection, one may further classify the closed operators in $\Lambda^{[i]}$ as those which are adjoint of a closed operator present in $T^{[i]}$. Rest of the closed operators are adjoints of some operator present in $H_{eff}^{[i]}$. It should be noted that $H_{eff}^{[i]}$ includes diagonal operators (all i-valence spectator scatterings) and $\Lambda^{[i]}$ includes these operators as well.

Before giving explicit expression for the functional, certain abbreviations are introduced. We denote the set of cluster amplitudes for all valence sectors by T, the set of effective Hamiltonian for all valence sectors by H_{eff}, and set of all Lagrange multipliers by Λ. We refer by C_A and $\tilde{C}_A$ the set of right hand and left hand side eigenvectors of highest valence sector effective Hamiltonian corresponding to a given state A, and its energy (the Lagrange multiplier corresponding to biorthogonality conditions on C_A and $\tilde{C}_A$) by E_A. As usual, all these quantities are collectively referred to as $\mathbf{\Theta}$.

$$T = \left\{ T^{[i]} \ \forall i = 0, \ldots, n \right\} \tag{5.15.1}$$

$$H_{eff} = \left\{ H_{eff}^{[i]} \ \forall i = 0, \ldots, n \right\} \tag{5.15.2}$$

$$\Lambda = \left\{ \Lambda^{[i]} \ \forall i = 0, \ldots, n \right\} \tag{5.15.3}$$

$$\tilde{C}_A = \left\{ \tilde{C}_{A\mu}^{[n]} \ \forall \mu = 1, \ldots, \dim(P^{[n]}) \right\} \tag{5.15.4}$$

$$\mathbf{\Theta} = \left\{ T, H_{eff}, \Lambda, C_A, \tilde{C}_A, E_A \right\} \tag{5.15.5}$$

For a specific i-valence sector, we denote the collection of all lower valence cluster amplitudes and effective Hamiltonian by $\tilde{T}^{[i]}$ and $\tilde{H}_{eff}^{[i]}$ respectively.

$$\tilde{T}^{[i]} = \left\{ T^{[m]} \ \forall m = 0, \ldots, i \right\} \tag{5.16.1}$$

$$\tilde{H}_{eff}^{[i]} = \left\{ H_{eff}^{[m]} \ \forall m = 0, \ldots, i \right\} \tag{5.16.2}$$

Using above abbreviations, constrained variation functional for a specific state of n-valence sector can be compactly written as,

$$\begin{aligned}\mathcal{J}(\Theta) &= \sum_{\mu,\nu} \tilde{C}^{[n]}_{A\nu} C^{[n]}_{\mu A} H^{\nu\mu\,[n]}_{eff} + \sum_{i=0}^{n} \mathcal{M}^{[i]}\big(\tilde{T}^{[i]}, \tilde{H}^{[i]}_{eff}, \Lambda^{[i]}\big) \\ &\quad - E_A\Big(\sum_{\mu} \tilde{C}^{[n]}_{A\mu} C^{[n]}_{\mu A} - 1\Big)\end{aligned} \tag{5.17}$$

$$\begin{aligned}\mathcal{M}^{[i]}\big(\tilde{T}^{[i]}, \tilde{H}^{[i]}_{eff}, \Lambda^{[i]}\big) &= \sum_{\mu,l} \langle \Phi^{[i]}_{\mu} | \Lambda^{[i]} | \chi^{[i]}_{l} \rangle \langle \chi^{[i]}_{l} | \Big(\overline{H\Omega} - \overline{\Omega H}_{eff}\Big)^{[i]} | \Phi^{[i]}_{\mu} \rangle \\ &\quad + \sum_{\mu,\nu} \langle \Phi^{[i]}_{\mu} | \Lambda^{[i]} | \Phi^{[i]}_{\nu} \rangle \langle \Phi^{[i]}_{\nu} | \Big(\overline{H\Omega} - \overline{\Omega H}_{eff}\Big)^{[i]} | \Phi^{[i]}_{\mu} \rangle\end{aligned} \tag{5.18}$$

Or by using resolution of identity for i-valence level, $\mathcal{M}^{[i]}$ can be simply written as,

$$\mathcal{M}^{[i]}\big(\tilde{T}^{[i]}, \tilde{H}^{[i]}_{eff}, \Lambda^{[i]}\big) = \sum_{\mu} \langle \Phi^{[i]}_{\mu} | \Lambda^{[i]} \Big(\overline{H\Omega} - \overline{\Omega H}_{eff}\Big)^{[i]} | \Phi^{[i]}_{\mu} \rangle \tag{5.19}$$

Stationarity condition on this functional with respect to variations in cluster amplitudes and effective Hamiltonian elements leads to the following equations for Lagrange multipliers,

$$\sum_{k=i}^{n} \frac{\delta \mathcal{M}^{[k]}}{\delta T^{[i]}} = 0 \tag{5.20}$$

$$\delta^{n}_{i} \tilde{C}^{[n]}_{A\nu} C^{[n]}_{\mu A} + \sum_{k=i}^{n} \frac{\delta \mathcal{M}^{[k]}}{\delta H^{\nu\mu\,[i]}_{eff}} = 0 \tag{5.21}$$

Here, δ^{n}_{i} is the standard Kronecker delta function. These equations require further analysis to make their structure clear. First of all, it is important to note the summation restrictions in above equations. This is a result of subsystem embedding condition (SEC) decoupling present in VUMRCC Eq (5.8)-(5.9). Since an i-valence cluster amplitude or effective Hamiltonian element does not occur in lower valence sector equations, the summation is restricted to higher valence sectors where such quantities appear. Therefore, to calculate Lagrange multipliers for a specific i-valence sector, Lagrange multipliers for higher valence sectors are necessary. The above equations will have to be solved in a specific order. Initially, the highest valence sector Lagrange multipliers $\Lambda^{[n]}$ are solved. In the next step, these $\Lambda^{[n]}$ are used to solve for $\Lambda^{[n-1]}$. This is continued till $\Lambda^{[0]}$ is reached. It is interesting to note that this decoupling is just the reverse of decoupling due to SEC.

Second aspect is that the equations for all sectors, expect for the highest sector, appear to be homogenous linear equations. However this is not so when this decoupling is considered. In the equations determining $\Lambda^{[i]}$, all the higher valence Lagrange multipliers are frozen in their value and hence they move to the inhomogeneous part of the equations. It should be noted that inhomogeneous part of lower valence Λ equations does not explicitly depend on model space coefficients. Instead this dependence enters implicitly through highest valence sector $\Lambda^{[n]}$ which is explicitly dependent on model space coefficients present in its inhomogeneous part. For the highest valence sector, non-zero inhomogeneous parts are only present in equations defining the closed part of $\Lambda^{[n]}$. Both open and closed parts of Lagrange multiplier for each valence sectors are coupled.

Appearance of closed parts in Lagrange multipliers in state-universal and valence-universal MRCC theories can be attributed to two reasons. One is the incompleteness of the model space and other is non-availability of explicit expression for effective Hamiltonian in terms of cluster operators. It must be mentioned here that closed parts of Lagrange multipliers generated by effective Hamiltonian can be eliminated in principle.

For example, in similarity transformation based approaches, effective Hamiltonian is always defined explicitly in terms of cluster amplitudes. In such a case, it is clear that closed parts in Lagrange multipliers generated by effective Hamiltonian are automatically eliminated in the functional itself and hence only those generated by cluster operators remain. However, in Bloch equation based approaches as is used here, effective Hamiltonian needs to be considered as an independent element and hence is solved along with cluster amplitudes. Assuming that analytic inverse of $P\Omega P$ is available, explicit expression for effective Hamiltonian can be constructed in principle. This can be substituted in cluster amplitude equations to obtain new equations independent of effective Hamiltonian. This again results in elimination of closed parts of Lagrange multipliers generated by effective Hamiltonian. However, such an inverse is not available in practice and hence explicit expression for effective Hamiltonian can not be constructed in general. This inevitably leads to further closed Lagrange multipliers.

V.3.3 Simplifications for special classes of model spaces

Although a general IMS is well suited to avoid intruder state problems associated with CMS, it has been realized that its use is often cumbersome due to many reasons. When using a general IMS, the second quantized operators can not be classified as open and closed operators based on their orbital labels alone.[12] This makes diagrammatic representation of algebraic equations much more difficult and book-keeping of terms becomes complex. However, for CMS and quasi-complete model spaces (QCMS), familiar diagrammatic methods are always available. In fact, QCMS of Lindgren[7] are perceived as the best compromise from this view point, as they are general enough to potentially avoid intruder state problems while retaining possibility of diagrammatic representation.

For CMS and QCMS, the constrained variational approach presented in the above subsections can be simplified by carrying out algebraic differentiation diagrammatically. Thus, Λ equations can be obtained by first drawing all the closed diagrams of the functional and considering open diagrams resulting from deleting a vertex representing a T or H_{eff} operator.

However, for CMS and some special classes of QCMS, there are further simplifications possible in the form of the functional itself. For CMS, due to intermediate normalization, there are no closed operators in Λ which are generated by cluster operator and all closed operators are generated by H_{eff}. Furthermore, H_{eff} is explicitly defined in terms of cluster amplitudes. In this case, it can be easily shown that Eq (5.13) or Eq (5.21) explicitly define closed amplitudes of Λ in terms of open amplitudes of Λ, T, C_A and $\tilde{C}_A$. When this relation is substituted in the functional, presence of H_{eff} is replaced by its explicit expression in terms of T. Hence, for CMS, the functional reduces to the one used by Szalay[26] for the valence-universal case, and to the one used in the third chapter for the state-universal case. Equations for Λ are obtained by differentiating the functional with respect to only T.

It is easy to see that this reduction in form of the functional, resulting from absence of closed amplitudes in Λ, happens only when effective Hamiltonian definition is explicit and non-recursive. While this automatically happens for CMS, it is not possible in general for QCMS. However, there are some special QCMS in VUMRCC where it turns out that, despite absence of intermediate normalization, effective Hamiltonian definition is explicit. The same holds true for special classes of model spaces in SUMRCC discussed by Meissner and coworkers,[16a] and are similar to QCMS discussed in VUMRCC theories. One valence particle-hole model space used for calculation of excitation energies in VUMRCC, the [1,1] Fock-space sector, is an example of this. In this case, it has been shown that equations corresponding to one-body part of cluster operator (referred to as de-excitations leading back to vacuum Φ) completely decouple from the rest of the equations and are not needed when only energy is to be calculated.[15,20] Since there are no products of cluster operators which are closed in [1,1] sector with each of them being connectable to H_{eff}, effective Hamiltonian is explicitly defined in terms of cluster amplitudes leading to simplifications in the form of functional as well as in procedure to obtain Λ equations. However, for higher valence particle-hole QCMS sectors, it is known that such a simplification is not possible in general.[15]

Meissner[29] has proposed a different formulation of VUMRCC based on hole–particle QCMS, based on earlier work of similarity transformations in Fock-space.[30] His approach generalizes the decoupling observed for [1,1] sector for higher sectors. It is well-known that the effective Hamiltonian computed for [1,1] sector is not a true effective Hamiltonian in its original sense, since it provides only the exact energies and not the exact wave-functions. In fact, as discussed by Mukherjee and co-workers,[15] it is referred to as effective Louvillian. It has been observed that the original formulation of VUMRCC using normal-ordered ansatz or otherwise, includes more number of cluster amplitudes than will be necessary for computation of energies alone.[12,31] The VUMRCC formulation of Meissner can be seen as a systematic way to eliminate these unnecessary cluster amplitudes for the case of hole–particle QCMS using a normal-ordered ansatz. As pointed out by Meissner,[29] and also by Nooijen,[30b] intermediate normalization is restored for the effective Hamiltonian (Louvillian). Therefore, for all sectors, it can be explicitly defined in terms of cluster amplitudes. When one is interested in only energy derivatives using hole–particle QCMS (not for general IMS), it appears that a CVA based on VUMRCC formulation of Meissner should be better suited. Since [1,1] sector decoupling has already been achieved, this becomes relevant only when higher hole–particle QCMS sectors are considered.

V.4 Higher-order molecular properties in valence-universal MRCC

In this section, the CVA for VUMRCC formulated in section V.3.2 is pursued further, and applied to [0,1], [1,0] and [1,1] Fock-space sector model spaces. As mentioned earlier, these model spaces have been extensively used in literature for obtaining, respectively, the ionization potentials (IP), electron affinities (EA) and excitation energies (EE) of closed shell systems.[19-22] The one valence-hole [0,1] sector model space is obtained by considering the determinants formed by deleting a valence electron (or creating a valence-hole) from vacuum Φ. Similarly, the one valence-particle [0,1] sector model space is obtained by adding a valence electron (or creating a valence-particle) to Φ. The one valence hole-particle [1,1] sector model space is obtained by creating a valence particle-hole pair in Φ. Alternatively, [0,1] and [1,0] sectors model spaces are also generated in a subduction process starting from [1,1] sector model space . While [0,1] and [1,0] sectors are CMS, [1,1] is a special QCMS.

An analytic response approach for valence-universal MRCC to obtain first-order molecular properties has been initiated by Pal,[24] closely following corresponding work of Monkhorst[32] for SRCC. Specific expressions for first-order molecular properties have been derived for [0,1], [1,0] and [1,1] Fock-space sectors. Applications have also been carried out in recent years to calculate dipole moments of open shell radicals and excited states of several molecules.[25]

However, as mentioned earlier, these developments do not include the benefits of Z-vector and similar developments of SRCC.[33-34] As a result, first-order response of cluster amplitudes is explicitly calculated. Efforts to towards efficient computation of molecular properties in MRCC were initiated by Szalay,[26] who, using CVA, analyzed relative cost of MRCC gradient calculations. An attempt to extend the Z-vector method for VUMRCC theories was done by Ajitha and Pal[35] by considering [0,1] sector as an example. Unlike the state-dependent approach of Szalay, their aim was to eliminate first-order response of cluster amplitude in first-order response of effective Hamiltonian to define a state-independent Z-vector. However, inversion of first-order response equations for cluster amplitudes in a form suitable for back-substitution could not be effected in general. Hence, their approach was not particularly successful and elimination could be effected only in some special cases.

Here, time-independent analytic response approach is applied to simplified form of constrained variation functionals for [0,1], [1,0] and [1,1] Fock-space sectors obtained in previous section. Simplified generic expressions for up to third-order molecular properties for a specific state in each of these sectors are derived using $(2n+1)$ and $(2n+2)$ rules.[28] Since [0,1] and [1,0] sector expressions are very similar to each other, we consider only [0,1] and [1,1] sectors. [1,0] sector expressions can be obtained by just changed the labels of [0,1] sector.

As discussed in section V.3.3, the constrained variation functional corresponding to a specific state in [0,1] and [1,1] sectors can be derived by eliminating all closed Lagrange multipliers for the sector being considered and all lower sectors. The resulting functionals are identical to those used by Szalay.[26] To facilitate compact representation of the functional and resulting expressions for molecular properties, we introduce the following abbreviations. The VUMRCC equations and effective Hamiltonian for [0,1] sector are compactly represented as shown below. Similar abbreviations are assumed for [0,0], [1,0] and [1,1] Fock-space sectors, and for the open parts of Lagrange multipliers.

$$\mathcal{W}_l^{[0,1]}(\mu) = \langle \chi_l^{[0,1]} | \left(\overline{H\Omega} - \overline{\Omega H}_{eff}\right)^{[0,1]} | \Phi_\mu^{[0,1]} \rangle = 0 \quad \forall \Phi_\mu^{[0,1]}, \chi_l^{[0,1]} \tag{5.22}$$

$$H_{eff}^{\nu\mu^{[0,1]}} = \langle \Phi_\nu^{[0,1]} | \left(\overline{H\Omega}\right)^{[0,1]} | \Phi_\mu^{[0,1]} \rangle \quad \forall \Phi_\mu^{[0,1]}, \Phi_\nu^{[0,1]} \tag{5.23}$$

$$\lambda_l^{[0,1]}(\mu) = \langle \Phi_\mu^{[0,1]} | \Lambda^{[0,1]} | \chi_l^{[0,1]} \rangle \quad \forall \Phi_\mu^{[0,1]}, \chi_l^{[0,1]} \tag{5.24}$$

The functional for a specific state A in [0,1] Fock-space sector can be written as,

$$\begin{aligned} \mathcal{J}(\Theta) = {} & \sum_{\mu,\nu} \tilde{C}_{A\nu}^{[0,1]} H_{eff}^{\nu\mu^{[0,1]}} C_{\mu A}^{[0,1]} + \sum_{l,\mu} \lambda_l^{[0,1]}(\mu) \mathcal{W}_l^{[0,1]}(\mu) + \\ & \sum_{l} \lambda_l^{[0,0]} \mathcal{W}_l^{[0,0]} - E_A \left(\sum_{\mu} \tilde{C}_{A\mu}^{[0,1]} C_{\mu A}^{[0,1]} - 1 \right) \end{aligned} \tag{5.25}$$

Similarly, the functional for a specific state in [1,1] Fock-space sector can be written as,

$$\begin{aligned} \mathcal{J}(\Theta) = {} & \sum_{\mu,\nu} \tilde{C}_{A\nu}^{[1,1]} H_{eff}^{\nu\mu^{[1,1]}} C_{\mu A}^{[1,1]} + \sum_{l,\mu} \lambda_l^{[1,1]}(\mu) \mathcal{W}_l^{[1,1]}(\mu) + \\ & \sum_{l,\mu} \lambda_l^{[0,1]}(\mu) \mathcal{W}_l^{[0,1]}(\mu) + \sum_{l,\mu} \lambda_l^{[1,0]}(\mu) \mathcal{W}_l^{[1,0]}(\mu) + \\ & \sum_{l} \lambda_l^{[0,0]} \mathcal{W}_l^{[0,0]} - E_A \left(\sum_{\mu} \tilde{C}_{A\mu}^{[1,1]} C_{\mu A}^{[1,1]} - 1 \right) \end{aligned} \tag{5.26}$$

It should be noted that, now $\mathbf{\Theta}$ does not include H_{eff} and includes only T and Λ of the highest sector being considered and all their lower-valence counterparts. It also includes C_A, $\tilde{C}_A$ and E_A of the highest sector.

V.4.1 The [0,1] and [1,1] sector response equations and simplified expressions for up to third-order molecular properties

The Λ equation is the only new equation among zeroth-order equations resulting from application of analytic response approach to [0,1] sector functional. As discussed in V.3.2 these equations are decoupled in the reverse order of SEC decoupling and lead to following inhomogeneous linear equations which have to be solved in the same order.

$$\sum_{q,\eta} \lambda_q^{[0,1]}(\eta)\left[\mathcal{W}_q^{[0,1]}(\eta)\right]_{\tau_l^{[0,1]}(\mu)} = -\sum_{\zeta,\eta} \tilde{C}_{A\varsigma}^{[0,1]} C_{\eta A}^{[0,1]} \left[H_{eff}^{\zeta\eta^{[0,1]}}\right]_{\tau_l^{[0,1]}(\mu)} \quad \forall l,\mu \tag{5.27}$$

$$\begin{aligned}\sum_{q} \lambda_q^{[0,0]}\left[\mathcal{W}_q^{[0,0]}\right]_{\tau_l^{[0,0]}} = &-\sum_{\xi,\eta} \tilde{C}_{A\varsigma}^{[0,1]} C_{\eta A}^{[0,1]} \left[H_{eff}^{\zeta\eta^{[0,1]}}\right]_{\tau_l^{[0,0]}} \\ &-\sum_{q,\eta} \lambda_q^{[0,1]}(\eta)\left[\mathcal{W}_q^{[0,1]}(\eta)\right]_{\tau_l^{[0,0]}} \quad \forall l\end{aligned} \tag{5.28}$$

Here, subscripts $\tau_l^{[0,1]}(\mu)$ and $\tau_l^{[0,0]}$ indicate differentiation of expression in square brackets with respect to cluster amplitudes $t_l^{[0,1]}(\mu) \equiv \langle \chi_l^{[0,1]} | T^{[0,1]} | \Phi_\mu^{[0,1]} \rangle$ and $t_l^{[0,0]} \equiv \langle \chi_l^{[0,0]} | T^{[0,0]} | \Phi^{[0,0]} \rangle$ respectively, and τ is the hole-particle excitation operator associated with the corresponding cluster-amplitude. The quantities within square brackets on the homogenous side of these equations are diagonal blocks of VUMRCC Jacobian matrix. They play important role for higher derivatives as well. The quantity within square brackets in the second term of inhomogeneous part of Eq (5.28) is non-diagonal block of Jacobian matrix. Therefore, $\Lambda^{[0,0]}$ is coupled to $\Lambda^{[0,1]}$ through non-diagonal block of Jacobian matrix. Diagrammatic expressions for above equations will be given in the next section. Here, we note that homogenous part of $\Lambda^{[0,0]}$ Eq (5.28) is exactly same as homogeneous part of SRCC Z-vector equations presented by Salter and coworkers.[34] The inhomogeneous part is the only new term which causes coupling of these two sectors.

Zeroth-order quantities $\boldsymbol{\Theta}$ are sufficient only for calculating first-order response properties. For higher order response properties, first-order quantities $\boldsymbol{\Theta}^{(1)}$ are required in addition. They are obtaining by making $\mathcal{J}^{(1)}$ stationary with respect to variations in $\boldsymbol{\Theta}$.

$$\frac{\delta \mathcal{J}^{(1)}}{\delta \boldsymbol{\Theta}} = 0 \tag{5.29}$$

Detailed expression for $\mathcal{J}^{(1)}$ in terms of $\boldsymbol{\Theta}$ and $\boldsymbol{\Theta}^{(1)}$ for [0,1] and [1,1] sector can be easily derived as in the third chapter, by expanding the constrained variation functionals in Eq (5.25)-(5.26) using Taylor series. This procedure leads to the following equations for first-order quantities $\boldsymbol{\Theta}^{(1)}$.

$$\sum_{q} \left[\mathcal{W}_l^{[0,0]} \right]_{\tau_q^{[0,0]}} t_q^{[0,0]^{(1)}} = -\left[\mathcal{W}_l^{[0,0]} \right]_{H \to H^{(1)}} \quad \forall l \tag{5.30}$$

$$\begin{aligned} \sum_{q,\eta} \left[\mathcal{W}_l^{[0,1]}(\mu) \right]_{\tau_q^{[0,1]}(\eta)} t_q^{[0,1]}(\eta)^{(1)} = &-\left[\mathcal{W}_l^{[0,0]}(\mu) \right]_{H \to H^{(1)}} \\ &-\sum_{q} \left[\mathcal{W}_l^{[0,0]}(\mu) \right]_{\tau_q^{[0,0]}} t_q^{[0,0]^{(1)}} \quad \forall l, \mu \end{aligned} \tag{5.31}$$

$$\sum_{\mu} \left\{ C_{\mu A}^{[0,1]^{(1)}} H_{eff}^{\nu\mu^{[0,1]}} + C_{\mu A}^{[0,1]} H_{eff}^{\nu\mu^{[0,1]^{(1)}}} \right\} = E_A^{[0,1]^{(1)}} C_{\nu A}^{[0,1]} + E_A^{[0,1]} C_{\nu A}^{[0,1]^{(1)}} \quad \forall \nu \tag{5.32}$$

$$\sum_{\nu} \left\{ \tilde{C}_{A\nu}^{[0,1]^{(1)}} H_{eff}^{\nu\mu^{[0,1]}} + \tilde{C}_{A\nu}^{[0,1]} H_{eff}^{\nu\mu^{[0,1]^{(1)}}} \right\} = E_A^{[0,1]^{(1)}} C_{A\mu}^{[0,1]} + E_A^{[0,1]} C_{A\mu}^{[0,1]^{(1)}} \quad \forall \mu \tag{5.33}$$

$$\sum_{\mu} \tilde{C}_{A\mu}^{[0,1]^{(1)}} C_{\mu A}^{[0,1]} + \tilde{C}_{A\mu}^{[0,1]} C_{\mu A}^{[0,1]^{(1)}} = 0 \tag{5.34}$$

$$\begin{aligned} \sum_{q,\eta} \lambda_q^{[0,1]}(\eta)^{(1)} \left[\mathcal{W}_q^{[0,1]}(\eta) \right]_{\tau_l^{[0,1]}(\mu)} &= -\sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(1)} \right]_{\tau_l^{[0,1]}(\mu)} \\ &-\sum_{\zeta,\eta} \left\{ \tilde{C}_{A\varsigma}^{[0,1]^{(1)}} C_{\eta A}^{[0,1]} + \tilde{C}_{A\varsigma}^{[0,1]} C_{\eta A}^{[0,1]^{(1)}} \right\} \left[H_{eff}^{\zeta\eta^{[0,1]}} \right]_{\tau_l^{[0,1]}(\mu)} \\ &-\sum_{\zeta,\eta} \tilde{C}_{A\varsigma}^{[0,1]} C_{\eta A}^{[0,1]} \left[H_{eff}^{\zeta\eta^{[0,1]^{(1)}}} \right]_{\tau_l^{[0,1]}(\mu)} \quad \forall l, \mu \end{aligned} \tag{5.35}$$

$$\begin{aligned}
&\sum_{q} \lambda_q^{[0,0]^{(1)}} \left[\mathcal{W}_q^{[0,0]} \right]_{\tau_l^{[0,0]}} = -\sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(1)} \right]_{\tau_l^{[0,0]}} \\
&-\sum_{q,\eta} \lambda_q^{[0,1]}(\eta)^{(1)} \left[\mathcal{W}_q^{[0,1]}(\eta) \right]_{\tau_l^{[0,0]}} - \sum_{q} \lambda_q^{[0,0]} \left[\mathcal{W}_q^{[0,0]^{(1)}} \right]_{\tau_l^{[0,0]}} \\
&-\sum_{\zeta,\eta} \left\{ \tilde{C}_{A\varsigma}^{[0,1]^{(1)}} C_{\eta A}^{[0,1]} + \tilde{C}_{A\varsigma}^{[0,1]} C_{\eta A}^{[0,1]^{(1)}} \right\} \left[H_{eff}^{\zeta\eta^{[0,1]}} \right]_{\tau_l^{[0,1]}} \\
&-\sum_{\zeta,\eta} \tilde{C}_{A\varsigma}^{[0,1]} C_{\eta A}^{[0,1]} \left[H_{eff}^{\zeta\eta^{[0,1]^{(1)}}} \right]_{\tau_l^{[0,1]}} \quad \forall l
\end{aligned} \tag{5.36}$$

In Eq (5.30)-(5.31), the subscript $H \rightarrow H^{(1)}$ refers to replacement of Hamiltonian $\hat{H}$ by field perturbation operator $\hat{H}^{(1)}$ within the expressions in square brackets. These equations should be solved sequentially in order they are presented. Eq (5.35)-(5.36) for $\Lambda^{(1)}$ are very similar to Eq (5.27)-(5.28). They are decoupled in exactly the same way and $\Lambda^{[0,0]^{(1)}}$ depends on $\Lambda^{[0,1]^{(1)}}$ through the same off-diagonal Jacobian block. Furthermore, their homogenous part contain exactly the same diagonal blocks of Jacobian. They only differ in their inhomogeneous parts. This means that $\Lambda^{(1)}$ equations can be solved by using the same computer program used for solving Λ by just modifying its inhomogeneous part appropriately. This in general holds true for higher-order response of Λ as well. While inhomogeneous parts of $\Lambda^{(1)}$ do depend on Λ, it is interesting to note that this dependence is only partial. Equations for $\Lambda^{[0,1]^{(1)}}$ depend only on $\Lambda^{[0,1]}$, and not on $\Lambda^{[0,0]}$. This may appear surprising at first sight; however, this is yet another consequence of SEC decoupling.

A similarity between $T^{(1)}$ and $\Lambda^{(1)}$ equations also needs to be pointed out. They share the same diagonal Jacobian blocks, except that the Jacobian enters as transpose in $\Lambda^{(1)}$ equation. This structure has already been pointed out in the third chapter and has been observed by Koch and coworkers in SRCC.[28b] Again this holds true in general for higher-order response as well. In VUMRCC, this correspondence holds separately for each sector. In actual computations, this Jacobian is not directly constructed except for small basis sets. Hence, the above similarity does not transform into any significant computational advantage.

The equations for various response quantities of a specific state in [1,1] Fock-space sector are obtained by applying stationarity condition on the corresponding functional and its first derivative is obtained using Taylor series expansion. The zeroth-order equations for $\Lambda^{[1,1]}$ are given below.

$$\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)\left[\mathcal{W}_q^{[1,1]}(\eta)\right]_{\tau_l^{[1,1]}(\mu)}=-\sum_{\zeta,\eta}\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]}\left[H_{eff}^{\zeta\eta^{[1,1]}}\right]_{\tau_l^{[1,1]}(\mu)}\quad\forall l,\mu \tag{5.37}$$

$$\begin{aligned}\sum_{q,\eta}\lambda_q^{[0,1]}(\eta)\left[\mathcal{W}_q^{[0,1]}(\eta)\right]_{\tau_l^{[0,1]}(\mu)}&=-\sum_{\zeta,\eta}\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]}\left[H_{eff}^{\zeta\eta^{[1,1]}}\right]_{\tau_l^{[0,1]}(\mu)}\\&\quad-\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)\left[\mathcal{W}_q^{[1,1]}(\eta)\right]_{\tau_l^{[0,1]}(\mu)}\quad\forall l,\mu\end{aligned} \tag{5.38}$$

$$\begin{aligned}&\sum_{q}\lambda_q^{[0,0]}\left[\mathcal{W}_q^{[0,0]}\right]_{\tau_l^{[0,0]}}=-\sum_{\xi,\eta}\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]}\left[H_{eff}^{\zeta\eta^{[1,1]}}\right]_{\tau_l^{[0,0]}}\\&-\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)\left[\mathcal{W}_q^{[1,1]}(\eta)\right]_{\tau_l^{[0,0]}}-\sum_{q,\eta}\lambda_q^{[0,1]}(\eta)\left[\mathcal{W}_q^{[0,1]}(\eta)\right]_{\tau_l^{[0,0]}}\\&-\sum_{q,\eta}\lambda_q^{[1,0]}(\eta)\left[\mathcal{W}_q^{[1,0]}(\eta)\right]_{\tau_l^{[0,0]}}\quad\forall l\end{aligned} \tag{5.39}$$

Along with Eq (5.38), equations for $\Lambda^{[1,0]}$ will also have to be solved, and this can be obtained by changing the sector labels. Apart from the common feature of decoupling, Eq (5.37)-(5.39) for $\Lambda^{[1,1]}$have lot of terms common with Eq (5.27)-(5.28) for $\Lambda^{[0,1]}$. The homogenous part of these lower sector equations is exactly same as before and even among inhomogeneous terms there are several common terms. Inhomogeneous terms of Eq (5.39) coupling $\Lambda^{[0,1]}$ and $\Lambda^{[1,0]}$ to $\Lambda^{[0,0]}$ are exactly same as in Eq (5.28). It can be concluded that the same routines which were used for homogeneous terms of [0,1], [1,0], and [0,0] sector as well as the routines used for calculating inhomogeneous terms coupling [0,1] and [1,0] sectors to [0,0] sector can be used for computing most of the terms in [1,1] sector response equations.

We complete analysis by presenting first-order response equations for [1,1] sector. Nothing new appears in $T^{(1)}$ equations where, in addition to Eq (5.30)-(5.31), equation for $T^{[1,1]^{(1)}}$ is obtained. The $C_A^{[1,1]^{(1)}}$ and $\tilde{C}_A^{[1,1]^{(1)}}$ similar to [0,1] sector counterparts Eq (5.32)-(5.34) with sector labels changed to [1,1]. Equations for $\Lambda^{(1)}$ are given below.

$$\begin{aligned}
&\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)^{(1)}\left[\mathcal{W}_q^{[1,1]}(\eta)\right]_{\tau_l^{[1,1]}(\mu)} = -\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)\left[\mathcal{W}_q^{[1,1]}(\eta)^{(1)}\right]_{\tau_l^{[1,1]}(\mu)} \\
&-\sum_{\zeta,\eta}\left\{\tilde{C}_{A\varsigma}^{[1,1]^{(1)}}C_{\eta A}^{[1,1]}+\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]^{(1)}}\right\}\left[H_{eff}^{\zeta\eta^{[1,1]}}\right]_{\tau_l^{[1,1]}(\mu)} \\
&-\sum_{\zeta,\eta}\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]}\left[H_{eff}^{\zeta\eta^{[1,1]^{(1)}}}\right]_{\tau_l^{[1,1]}(\mu)} \qquad \forall l,\mu
\end{aligned} \tag{5.40}$$

$$\begin{aligned}
&\sum_{q,\eta}\lambda_q^{[0,1]}(\eta)^{(1)}\left[\mathcal{W}_q^{[0,1]}(\eta)\right]_{\tau_l^{[0,1]}(\mu)} = -\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)^{(1)}\left[\mathcal{W}_q^{[1,1]}(\eta)\right]_{\tau_l^{[0,1]}(\mu)} \\
&-\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)\left[\mathcal{W}_q^{[1,1]}(\eta)^{(1)}\right]_{\tau_l^{[0,1]}(\mu)} -\sum_{q,\eta}\lambda_q^{[0,1]}(\eta)\left[\mathcal{W}_q^{[0,1]}(\eta)^{(1)}\right]_{\tau_l^{[0,1]}(\mu)} \\
&-\sum_{\zeta,\eta}\left\{\tilde{C}_{A\varsigma}^{[1,1]^{(1)}}C_{\eta A}^{[1,1]}+\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]^{(1)}}\right\}\left[H_{eff}^{\zeta\eta^{[1,1]}}\right]_{\tau_l^{[0,1]}(\mu)} \\
&-\sum_{\zeta,\eta}\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]}\left[H_{eff}^{\zeta\eta^{[1,1]^{(1)}}}\right]_{\tau_l^{[0,1]}(\mu)} \qquad \forall l,\mu
\end{aligned} \tag{5.41}$$

$$\begin{aligned}
&\sum_{q}\lambda_q^{[0,0]^{(1)}}\left[\mathcal{W}_q^{[0,0]}\right]_{\tau_l^{[0,0]}} = -\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)\left[\mathcal{W}_q^{[1,1]}(\eta)^{(1)}\right]_{\tau_l^{[0,0]}} \\
&-\sum_{q,\eta}\lambda_q^{[1,1]}(\eta)^{(1)}\left[\mathcal{W}_q^{[1,1]}(\eta)\right]_{\tau_l^{[0,0]}} -\sum_{q,\eta}\lambda_q^{[0,1]}(\eta)\left[\mathcal{W}_q^{[0,1]}(\eta)^{(1)}\right]_{\tau_l^{[0,0]}} \\
&-\sum_{q,\eta}\lambda_q^{[0,1]}(\eta)^{(1)}\left[\mathcal{W}_q^{[0,1]}(\eta)\right]_{\tau_l^{[0,0]}} -\sum_{q,\eta}\lambda_q^{[1,0]}(\eta)\left[\mathcal{W}_q^{[1,0]}(\eta)^{(1)}\right]_{\tau_l^{[0,0]}} \\
&-\sum_{q,\eta}\lambda_q^{[0,1]}(\eta)^{(1)}\left[\mathcal{W}_q^{[0,1]}(\eta)\right]_{\tau_l^{[0,0]}} -\sum_{q}\lambda_q^{[0,0]}\left[\mathcal{W}_q^{[0,0]^{(1)}}\right]_{\tau_l^{[0,0]}} \\
&-\sum_{\zeta,\eta}\left\{\tilde{C}_{A\varsigma}^{[1,1]^{(1)}}C_{\eta A}^{[1,1]}+\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]^{(1)}}\right\}\left[H_{eff}^{\zeta\eta^{[1,1]}}\right]_{\tau_l^{[0,1]}} \\
&-\sum_{\zeta,\eta}\tilde{C}_{A\varsigma}^{[1,1]}C_{\eta A}^{[1,1]}\left[H_{eff}^{\zeta\eta^{[1,1]^{(1)}}}\right]_{\tau_l^{[0,1]}} \qquad \forall l
\end{aligned} \tag{5.42}$$

Here, the [1,0] sector counterpart of Eq (5.41) is present, although not written out explicitly. These equations illustrate a structure which can lead to computational feasibility and advantages. Firstly, as usual, homogenous part for each sector is the same as earlier. This implies that, in general, irrespective of the sector and the state that is targeted, the computer routine for homogenous part of a sector needs to be constructed only once and reused. Even among inhomogeneous part there are several terms in common. In Eq (5.41), non-diagonal Jacobian block of second term in inhomogeneous part which couples $\Lambda^{[0,1]^{(1)}}$ with $\Lambda^{[1,1]^{(1)}}$ already occurs in inhomogeneous part of Eq (5.38) and need not be reprogrammed. For same reasons, the second, fourth and sixth inhomogeneous terms in Eq (5.42) need not be reprogrammed. The third term of Eq (5.42) containing first-order Jacobian is same as the first inhomogeneous term in Eq (5.35) for $\Lambda^{[0,1]^{(1)}}$ obtained when [0,1] sector first-order response was considered. Again for same reasons, first, third and fifth terms of Eq (5.42) need not be reprogrammed. Hence, in each of the above equations, exactly one inhomogeneous term containing Λ needs to be programmed. Among the inhomogeneous terms depending on C_A and $\tilde{C}_A$, those containing $C_A^{[1,1]^{(1)}}$ or $\tilde{C}_A^{[1,1]^{(1)}}$ may be evaluated by the same routines used to construct similar inhomogeneous terms in zeroth-order response equations.

It should be noted that, for all the sectors considered, the state-dependency is restricted to inhomogeneous part of response equations. This is not of any use when only one state is considered at a time. However, when more than one state is considered at a time for property evaluation, as in curve-crossing studies of excited states using VUMRCC, this can lead to some computational benefits.

The zeroth and first-order response equations presented till now are sufficient to compute simplified expressions for up to third order molecular properties. As noted in the third chapter, energy derivative of n-th order, $E_A^{(1)}$, is the value of functional $\mathcal{J}^{(n)}$, denoted by $\mathcal{J}_{opt}^{(n)}$, when the stationary values of $\left\{\mathcal{J}^{(m)}\ \forall m = 0,\ldots,n\right\}$ are substituted in it. Hence, $\mathcal{J}_{opt}^{(n)}$ may be considered as the required energy derivative, allowing treatment of E_A as another Lagrange multiplier. As in the third chapter, we use the $(2n+1)$ and $(2n+2)$ rules to identify response quantities which are not needed for calculating property of a given order. The final simplified expressions for molecular properties of a specific state in [0,1] sector are given below.

$$\begin{aligned}\mathcal{J}_{opt}^{(1)} = &\sum_{\mu,\nu} \tilde{C}_{A\nu}^{[0,1]} C_{\mu A}^{[0,1]} \left[{H_{eff}^{\nu\mu}}^{[0,1]\,(1)} \right]_{T^{(0)}} + \sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(1)} \right]_{T^{(0)}} \\ &+ \sum_q \lambda_q^{[0,0]} \left[{\mathcal{W}_q^{[0,0]}}^{(1)} \right]_{T^{(0)}}\end{aligned} \tag{5.43}$$

$$\begin{aligned}\mathcal{J}_{opt}^{(2)} = &\sum_{\mu,\nu} \tilde{C}_{A\nu}^{[0,1]} C_{\mu A}^{[0,1]} \left[{H_{eff}^{\nu\mu}}^{[0,1]\,(2)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(2)} \right]_{T^{(1)}} \\ &+ \sum_q \lambda_q^{[0,0]} \left[{\mathcal{W}_q^{[0,0]}}^{(2)} \right]_{T^{(1)}} \\ &- 2\left(\sum_{\mu,\nu} {\tilde{C}_{A\nu}^{[0,1]}}{}^{(1)} {C_{\mu A}^{[0,1]}}{}^{(1)} {H_{eff}^{\nu\mu}}^{[0,1]} - E_A^{[0,1]} \sum_{\mu} {\tilde{C}_{A\mu}^{[0,1]}}{}^{(1)} {C_{\mu A}^{[0,1]}}{}^{(1)} \right)\end{aligned} \tag{5.44}$$

$$\begin{aligned}\mathcal{J}_{opt}^{(3)} = &\sum_{\mu,\nu} \tilde{C}_{A\nu}^{[0,1]} C_{\mu A}^{[0,1]} \left[{H_{eff}^{\nu\mu}}^{[0,1]\,(3)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(3)} \right]_{T^{(1)}} \\ &+ \sum_q \lambda_q^{[0,0]} \left[{\mathcal{W}_q^{[0,0]}}^{(3)} \right]_{T^{(1)}} + 3\sum_{q,\eta} \lambda_q^{[0,1]}(\eta)^{(1)} \left[\mathcal{W}_q^{[0,1]}(\eta)^{(2)} \right]_{T^{(1)}} \\ &+ 3\sum_q {\lambda_q^{[0,0]}}^{(1)} \left[{\mathcal{W}_q^{[0,0]}}^{(2)} \right]_{T^{(1)}} \\ &+ 6\left(\sum_{\mu,\nu} {\tilde{C}_{A\nu}^{[0,1]}}{}^{(1)} {C_{\mu A}^{[0,1]}}{}^{(1)} \left[{H_{eff}^{\nu\mu}}^{[0,1]\,(1)} \right]_{T^{(1)}} - {E_A^{[0,1]}}^{(1)} \sum_{\mu} {\tilde{C}_{A\mu}^{[0,1]}}{}^{(1)} {C_{\mu A}^{[0,1]}}{}^{(1)} \right) \\ &+ 3\left(\sum_{\mu,\nu} \left({\tilde{C}_{A\nu}^{[0,1]}}{}^{(1)} C_{\mu A}^{[0,1]} + \tilde{C}_{A\nu}^{[0,1]} {C_{\mu A}^{[0,1]}}{}^{(1)} \right) \left[{H_{eff}^{\nu\mu}}^{[0,1]\,(2)} \right]_{T^{(1)}} \right)\end{aligned} \tag{5.45}$$

For a specific state in [1,1] sector the following expressions are obtained.

$$\begin{aligned}\mathcal{J}_{opt}^{(1)} &= \sum_{\mu,\nu} \tilde{C}_{A\nu}^{[1,1]} C_{\mu A}^{[1,1]} \left[{H_{eff}^{\nu\mu}}^{[1,1]\,(1)} \right]_{T^{(0)}} + \sum_{q,\eta} \lambda_q^{[1,1]}(\eta) \left[\mathcal{W}_q^{[1,1]}(\eta)^{(1)} \right]_{T^{(0)}} \\ &+ \sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(1)} \right]_{T^{(0)}} + \sum_{q,\eta} \lambda_q^{[1,0]}(\eta) \left[\mathcal{W}_q^{[1,0]}(\eta)^{(1)} \right]_{T^{(0)}} \\ &+ \sum_{q} \lambda_q^{[0,0]} \left[{\mathcal{W}_q^{[0,0]}}^{(1)} \right]_{T^{(0)}}\end{aligned} \tag{5.46}$$

$$\begin{aligned}\mathcal{J}_{opt}^{(2)} &= \sum_{\mu,\nu} \tilde{C}_{A\nu}^{[1,1]} C_{\mu A}^{[1,1]} \left[{H_{eff}^{\nu\mu}}^{[1,1]\,(2)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q^{[1,1]}(\eta) \left[\mathcal{W}_q^{[1,1]}(\eta)^{(2)} \right]_{T^{(1)}} \\ &+ \sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(2)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q^{[1,0]}(\eta) \left[\mathcal{W}_q^{[1,0]}(\eta)^{(2)} \right]_{T^{(1)}} \\ &+ \sum_{q} \lambda_q^{[0,0]} \left[{\mathcal{W}_q^{[0,0]}}^{(2)} \right]_{T^{(1)}} \\ &- 2\left(\sum_{\mu,\nu} {\tilde{C}_{A\nu}^{[1,1]}}^{(1)} {C_{\mu A}^{[1,1]}}^{(1)} {H_{eff}^{\nu\mu}}^{[1,1]} - E_A^{[1,1]} \sum_{\mu} {\tilde{C}_{A\mu}^{[1,1]}}^{(1)} {C_{\mu A}^{[1,1]}}^{(1)} \right)\end{aligned} \tag{5.47}$$

$$\begin{aligned}\mathcal{J}_{opt}^{(3)} &= \sum_{\mu,\nu} \tilde{C}_{A\nu}^{[1,1]} C_{\mu A}^{[1,1]} \left[{H_{eff}^{\nu\mu}}^{[1,1]\,(3)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q^{[1,1]}(\eta) \left[\mathcal{W}_q^{[1,1]}(\eta)^{(3)} \right]_{T^{(1)}} \\ &+ \sum_{q,\eta} \lambda_q^{[0,1]}(\eta) \left[\mathcal{W}_q^{[0,1]}(\eta)^{(3)} \right]_{T^{(1)}} + \sum_{q,\eta} \lambda_q^{[1,0]}(\eta) \left[\mathcal{W}_q^{[1,0]}(\eta)^{(3)} \right]_{T^{(1)}} \\ &+ \sum_{q} \lambda_q^{[0,0]} \left[{\mathcal{W}_q^{[0,0]}}^{(3)} \right]_{T^{(1)}} + 3\sum_{q,\eta} \lambda_q^{[1,1]}(\eta)^{(1)} \left[\mathcal{W}_q^{[1,1]}(\eta)^{(2)} \right]_{T^{(1)}} \\ &+ 3\sum_{q,\eta} \lambda_q^{[0,1]}(\eta)^{(1)} \left[\mathcal{W}_q^{[0,1]}(\eta)^{(2)} \right]_{T^{(1)}} + 3\sum_{q,\eta} \lambda_q^{[1,0]}(\eta)^{(1)} \left[\mathcal{W}_q^{[1,0]}(\eta)^{(2)} \right]_{T^{(1)}} \\ &+ 3\sum_{q} {\lambda_q^{[0,0]}}^{(1)} \left[{\mathcal{W}_q^{[0,0]}}^{(2)} \right]_{T^{(1)}} \\ &+ 6\left(\sum_{\mu,\nu} {\tilde{C}_{A\nu}^{[1,1]}}^{(1)} {C_{\mu A}^{[1,1]}}^{(1)} \left[{H_{eff}^{\nu\mu}}^{[1,1]\,(1)} \right]_{T^{(1)}} - {E_A^{[1,1]}}^{(1)} \sum_{\mu} {\tilde{C}_{A\mu}^{[1,1]}}^{(1)} {C_{\mu A}^{[1,1]}}^{(1)} \right) \\ &+ 3\left(\sum_{\mu,\nu} \left({\tilde{C}_{A\nu}^{[1,1]}}^{(1)} C_{\mu A}^{[1,1]} + \tilde{C}_{A\nu}^{[1,1]} {C_{\mu A}^{[1,1]}}^{(1)} \right) \left[{H_{eff}^{\nu\mu}}^{[1,1]\,(2)} \right]_{T^{(1)}} \right)\end{aligned} \tag{5.48}$$

Here, subscript $T^{(n)}$ on a bracketed expression means that only terms containing $\left\{ T^{(m)} \quad \forall m = 0,\ldots,n \right\}$ have been retained in the bracketed expression.

V.4.2 Diagrammatic equations for first-order response properties

In this section, we present zeroth-order Lagrange multiplier equations in a diagrammatic form to enable efficient computation of first-order properties using

VUMRCC theory. The diagrammatic expressions for only [0,1] and [1,1] sectors are presented here. Expressions for [1,0] sector can be derived from [0,1] sector expressions by hole-particle reversal.[20] The [0,0] and [0,1] sectors are treated within singles and doubles approximation. For the [1,1] sector, as pointed out earlier, it is known that singles decouple completely from rest of the equations and need not be considered for energy calculations.[15,20] Therefore, only doubles are considered for this sector. The relevant diagrammatic expressions for cluster-amplitude equations have been taken from literature.[20]

Fig.V.1 shows various types of lines and vertices used in diagrammatic representation. As shown in Fig.V.1(a), single arrows indicate both active and inactive holes and particles, and double arrows represent only active holes or particles. A third type of arrow convenient in certain types of diagrams is also shown. They are referred to as dummy valence lines. Whenever a pair of ingoing and outgoing dummy valence lines occurs in a diagram, a summation over dummy valence labels is assumed. Fig.V.1(b) shows different kinds of vertices used for diagrammatic representation. Filled circles and open circles represent T and Λ respectively, and their forms for the sectors and truncations considered here are given in Fig.V.1(c) and (d). A circle with two crossed lines represents one-body and two-body part of Hamiltonian. It is known that various matrix elements of operator $\bar{H} = e^{-T^{[0,0]}} H_N e^{T^{[0,0]}}$ occur throughout VUMRCC theory.[20] It is useful to pre-compute $\bar{H}$, store it and use it in later expressions. One-body and two-body parts of $\bar{H}$ are represented by a circle filled with lines. Detailed expressions for matrix elements of $\bar{H}$ are available in literature.[36] Filled squares represent model space coefficients appearing in inhomogeneous parts of Lagrange multiplier equations. Filled square with lines only below the vertex represent $\tilde{C}_A$ and one with lines above the vertex represent C_A. Open squares represent H_{eff}. Both these vertices have only valence lines as shown in Fig.V.1(e). While vertices representing model space coefficients of [1,1] are number-conserving, those of [0,1] and [1,0] sectors are not number-conserving. Finally, a square with two crossed lines as in Fig.V.1(b) is a generic vertex.

Fig.V.2 and Fig.V.3 represent homogenous parts of $\Lambda^{[0,1]}$ and $\Lambda^{[1,1]}$ equations respectively. As discussed in the previous section, this part for a given sector is not dependent on whether it is the highest sector or not. While Fig.V.2(a) and (b) represent one-body part of $\Lambda^{[0,1]}$, Fig.V.2(c) and (d) represent two-body part. These diagrams have been expressed in terms of a generic vertex, whose structure is given in Fig.V.2(e). The final diagrammatic expressions are Fig.V.2(a)-(d) expanded after the insertion of this generic vertex into Fig.V.2(a) and (c). Likewise, for the [1,1] sector, the final expressions are Fig.V.3(a)-(b) expanded with insertion of generic vertex in Fig.V.3(c) into Fig.V.3(a). As noted earlier, homogenous part of $\Lambda^{[0,0]}$ are the same as the SRCC Z-vector equations and has been presented in detail by Salter and coworkers.[34]

In order to make the correspondence between algebraic equations and diagrams clear, as an example, we outline derivation of homogenous part of $\Lambda^{[0,1]}$ diagrammatic equations presented in Fig.V.2. From the discussions in previous section, it is clear that these terms arise from algebraic differentiation of terms of [0,1] sector functional containing $\Lambda^{[0,1]}$ with respect one and two-body amplitudes of $T^{[0,1]}$. The terms of functional contributing to this explicit differentiation are collected below.

$$\begin{aligned}&\sum_{\mu}\langle\Phi_{\mu}^{[0,1]}|\Lambda_1^{[0,1]}\left(\overline{H\Omega}\right)_1|\Phi_{\mu}^{[0,1]}\rangle+\sum_{\mu}\langle\Phi_{\mu}^{[0,1]}|\Lambda_2^{[0,1]}\left(\overline{H\Omega}\right)_2|\Phi_{\mu}^{[0,1]}\rangle\\&-\sum_{\mu}\langle\Phi_{\mu}^{[0,1]}|\Lambda_1^{[0,1]}\left(\overline{\Omega H_{eff}^{[0,1]}}\right)_1|\Phi_{\mu}^{[0,1]}\rangle-\sum_{\mu}\langle\Phi_{\mu}^{[0,1]}|\Lambda_2^{[0,1]}\left(\overline{\Omega H_{eff}^{[0,1]}}\right)_2|\Phi_{\mu}^{[0,1]}\rangle\end{aligned}\tag{5.49a}$$

$$H_{eff}^{[0,1]}=P^{[0,1]}\left(\overline{H\Omega}\right)_1P^{[0,1]}\tag{5.49b}$$

Here, subscripts indicate one and two-body parts of corresponding operators. Diagrammatic representation of these terms is obtained by closing [0,1] sector one and two-body diagrams with a corresponding Lagrange multiplier vertices. Although the resulting diagrams contain a pair of valence hole lines, their labels are not independent and they have to be equated and summed over. This amounts to selecting only diagonal parts of operators as indicated in above equation. For this purpose, diagrammatically we may represent such valence lines by dummy valence lines which automatically imply summation.

It is well-known that diagrammatic meaning of algebraic differentiation is to delete the vertex with respect to which differentiation is being carried out. Now consider different open diagrams obtained by deleting an one-body $T^{[0,1]}$-vertex. It is easy to see that, for every diagram resulting from first term of Eq (5.49a) there is one corresponding diagram coming from deletion of same vertex in $H_{eff}^{[0,1]}$ of third and fourth terms. All such diagrams can be collected into a single diagram as in Fig.V.2(a) by defining a generic vertex as in Fig.V.2(e). Similar method can be used to generate diagrams in Fig.V.2(c) for two-body terms using the same generic vertex. Diagrams in Fig.V.2(b) and (d) are obtained by deleting the $T^{[0,1]}$ vertex in second term as well as the $T^{[0,1]}$ vertex coming from Ω of $\overline{\Omega H_{eff}}^{[0,1]}$ in third and fourth terms. Essentially the same method can be applied to generate [1,1] sector diagrammatic equations in Fig.V.3 by defining appropriate generic vertices. The procedure can adapted for deriving the diagrams presented in other figures for identification of a generic vertex structures simplifying the diagrammatics.

It is well known in SRCC that Z-vector has a necessary disconnected structure which arises from certain disconnected terms in homogenous part of SRCC Z-vector equations.[34] The same can be expected for VUMRCC as well. In fact, Fig.V.2(c) for two-body part of $\Lambda^{[0,1]}$ indeed has one disconnected term which, upon iteration, leads to necessary disconnected contributions. However, homogenous part of $\Lambda^{[1,1]}$ does not contain disconnected terms. This is due to the complete decoupling of one-body amplitude equations of [1,1] sector from the two-body amplitude equations. It will be seen that inhomogeneous part, in general, contains disconnected terms eventually leading to disconnected terms in Λ.

All the inhomogeneous terms can be synthesized from the diagram templates presented in Fig.V.2-8, by inserting generic vertices with specific expressions and applying certain additional rules presented below. While inhomogeneous terms of the highest sector are relatively simple, for other sectors this is not so. As observed in previous section, the Λ of higher sectors enter inhomogeneous parts of lower sectors as frozen terms. Their number is large, specially for [0,0] sector which receives contributions from all the higher valence sectors. However, these terms are to be computed only once, and hence are not computationally expensive.

It is convenient to divide inhomogeneous terms into two groups. The first group depends explicitly on model space coefficients. These terms originate from deleting a T-vertex for the sector in question, in model space dependent part (containing H_{eff} of highest sector) of the functional. The second group does not depend explicitly on model space coefficients and it depends on Λ. An interesting aspect of this group is that it can be described without reference to the highest sector being considered. Therefore, the influence of [0,1] sector on [0,0] sector appearing in second group of terms, is the same whether the highest sector is [0,1] or [1,1]. This can be exploited to make to efficient reuse of computer routines for different sectors. This scheme will be particularly useful when states in higher sectors are considered.

To minimize the number of diagrams, we adopt following two conventions. 1. If there are any unlabelled lines a diagram, all possible diagrams obtained by labeling them in all possible ways keeping intact the nature of the vertices are also considered. 2. After substitution of a generic vertex into a diagram template, if there is a dummy valence line connected to Hamiltonian vertex from the bottom side, then an additional diagram should be considered where an appropriate $T^{[0,1]}$ or $T^{[1,0]}$ vertex is inserted in between Hamiltonian vertex and the dummy line, without increasing the number of lines. In the resulting diagram, the dummy line appears at the bottom of inserted T-vertex. Similarly, if there is more than one dummy line connected to Hamiltonian vertex from the bottom, this replacement should be carried out separately for each dummy line. If there is a pair of incoming and outgoing dummy lines connected to Hamiltonian vertex from the bottom, then an additional diagram obtained by inserting a $T^{[1,1]}$-vertex between the Hamiltonian vertex and the dummy line pair should also be considered. Wherever there is more than one diagram arising out of these two rules, the total number of resulting diagrams has been indicated in a parenthesis to the right of diagram template. These rules are applicable to generate second group of inhomogeneous terms. The second rule must be slightly modified when generating the first group of inhomogeneous terms. For these terms, instead of dummy valence lines, normal valence lines connecting to model-space coefficient vertices are present. The second rule should be applied to such valence lines. In both cases, the total number of diagrams obtained by application of these two rules on a diagram template does not change. Explicit application of these rules is illustrated in the following.

First, we discuss the second group of inhomogeneous terms. Such terms, for [0,0] sector, can be obtained from closed diagrams presented in Fig.V.4 and Fig.V.5. The required open diagrams corresponding to these inhomogeneous terms can be obtained by deleting a specific $T^{[0,0]}$ vertex. For obtaining these diagrams, we have expanded $\bar{H}$ and rearranged the terms. The second group of inhomogeneous terms arising from influence of [0,1] sector on [0,0] sector are obtained by inserting the generic vertex in Fig.V.4(c) and (d) into Fig.V.4(a) and considering, in addition, diagrams of Fig.V.5. While diagram templates in Fig.V.4(a) result from expansion of $\bar{H}$ occurring in one-body part of [0,1] sector cluster-amplitude equations, diagrams of Fig.V.5 come from two-body part of same equations. As an example to illustrate application of above rules, it is clear that diagram templates in Fig.V.5 or those obtained by the above insertion lead to closed diagrams with two down-going dummy valence-hole lines. For each of first three diagram templates in Fig.V.4(a), application of second rule gives only one additional diagram by inserting one-body part of $T^{[0,1]}$.

Second group of inhomogeneous terms of [0,0] sector arising from influence of [1,1] sector are obtained when Fig.V.7(a) is inserted with Fig.V.7(c)-(d), and Fig.V.8(a) is inserted with Fig.V.8(b). Diagrams in Fig.V.7 result from expansion of $\bar{H}$ occurring in two-body part of [1,1] sector cluster-amplitude equations. Since [1,1] sector equations contain terms connecting [0,1] and [1,0] sector effective Hamiltonian, this gives rise to additional diagrams as in Fig.V.8. Only the closed diagrams have been presented to avoid proliferation of number of diagrams. The corresponding open diagrams are easily obtained by deleting a $T^{[0,0]}$-vertex from these closed diagrams.

For the influence of [1,1] sector on [0,1] (and also [1,0] sector), second group of inhomogeneous terms are obtained by considering Fig.V.6(a)-(d) with insertion as in Fig.V.6(f). Since resulting diagrams are not many, we have chosen to present open diagrams rather than closed diagrams. In these diagrams, wherever possible $\bar{H}$ has been made use of, which will result in computational efficiency.

The first group of inhomogeneous terms are obtained from same diagram templates by carrying an insertion with a generic vertex containing model space coefficients and applying the rules mentioned above. Consider the [0,1] sector as the highest sector where the desired state resides. For $\Lambda^{[0,1]}$ equations, there are no second group of inhomogeneous terms and first group of terms are obtained by inserting Fig.V.2(f) into Fig.V.2(a) and (c). For $\Lambda^{[0,0]}$ equations, the relevant closed diagrams obtained when Fig.V.4(b) is inserted into Fig.V.4(a).

Similarly, when [1,1] sector is the highest sector, again there are no second group of terms in $\Lambda^{[1,1]}$ equations and first group of terms are obtained by inserting Fig.V.3(d) into Fig.V.3(a). For first group of terms in $\Lambda^{[0,1]}$ equations, insertion of Fig.V.6(e) into Fig.V.6(a) and (c) is needed. For $\Lambda^{[0,0]}$ equations, the insertion required is Fig.V.7(b) into Fig.V.7(a).

Specific diagrammatic expressions for first-order property are not presented here. They can be easily obtained by closing effective Hamiltonian and cluster-amplitude equation diagrams[20] as described below. Effective Hamiltonian diagrams of the highest sector are closed by joining at top and bottom with corresponding $\tilde{C}_A$ and C_A vertices respectively. This results in completely closed diagrams. The diagrams of cluster-amplitude equations for each sector including [0,0] (standard SRCC equations) sector, are closed by corresponding Λ vertex. Depending on the highest sector, this leads to closed diagrams with different number of pairs of incoming and outgoing dummy valence lines. These dummy lines are summed up as mentioned earlier. Finally, in all the resulting diagrams, occurrence of $\hat{H}$ vertex is replaced by $\hat{H}^{(1)}$ vertex.

As explained in the second chapter, to achieve further efficiency, simplification is carried out to express a first-order molecular property as a contraction of effective CC density matrices with $\hat{H}^{(1)}$. Effective MRCC density matrix is constructed using Λ and T. As suggested by Rice and Amos,[37] this contraction is efficiently carried out in atomic orbital (AO) basis thereby avoiding transformation of $\hat{H}^{(1)}$ into molecular-orbital (MO) basis for different modes of perturbation. This requires a single back-transformation of perturbation independent effective CC density matrix from MO to AO basis. The same approach can be followed here as well leading to construction of state-dependent effective MRCC density matrices similar to the ones derived in the second chapter.

Form of $\hat{H}^{(1)}$ depends on the nature of perturbation. For molecular electric properties, external electric field interacting with molecular dipole leads to a simple one-body perturbation when orbital relaxation effects are neglected. In this case, many diagrams drop out and molecular property expressions become simple. For the case of geometric perturbation leading to gradients and hessians of potential energy surfaces, both one and two body terms enter into $\hat{H}^{(1)}$.

For geometric perturbation, orbital relaxation effects need to be considered. Even for electric field perturbation, orbital relaxation effects are not negligible in many situations. Inclusion of orbital relaxation can be carried out in two ways. One way is to consider solution of first-order coupled-perturbed (CP) equations[38] defining first-order response of orbitals for each mode of perturbation. This is used to construct $\hat{H}^{(1)}$ explicitly including orbital relaxation effects. The advantage of directly computing perturbation dependent first-order orbital derivatives is that it is independent of MRCC parameters and the state considered. Computational effort for solution of CP equations is not significant as compared to th effort needed for solving T and Λ. The second approach, as described by Salter and coworkers in SRCC,[34] is a kind of Z-vector method which eliminates perturbation dependent first-order orbital derivatives in favor of a single perturbation independent quantity. While perturbation independence is a clear advantage, the disadvantage, at least for first-order properties, is that the equations defining this quantity are dependent on all MRCC parameters, Λ for the state being considered.

When calculating MRCC first-order response, interest is likely to be in at least a few states. If the number of states to be considered equals or exceeds the number of modes of perturbation, as can easily happen for electric-field perturbation with three modes, then second approach is unlikely to be useful for first-order properties. It will emerge to be useful when the number of modes of perturbation is significantly large enough to overcome the disadvantages of state-specificity of the perturbation independent quantity, as it can happen in molecules with many degrees of freedom. A generalization the second approach for inclusion of orbital response contributions in higher-order properties can be carried out by extending functional to include orbital response terms, as shown by Koch and coworkers.[28b] For first-order properties, further numerical comparison is required to decide between two alternatives.

V.5 Conclusions

The constrained variational procedure, discussed in the third chapter in context of CMS based SUMRCC, has been suitably generalized in this chapter for IMS based MRCC theories, both the state-universal as well as the valence-universal ones. The main result of this generalization is the appearance of closed parts in Lagrange multipliers, and need to make the constrained variation functional stationary with respect to effective Hamiltonian as well. Alternatively, this can also be seen as a consequence of the fact that, irrespective of the type of model space employed, effective Hamiltonian has to be considered as an independent parameter in Bloch equation based approaches. It happens that, for CMS and some special classes of model spaces, these closed parts can be conveniently related to open parts in a simple way.

This formulation has been applied to VUMRCC based on [0,1], [1,0] and [1,1] Fock-space sectors. The response equations up to first-order have been derived and simplified expressions for up to third-order molecular properties have been obtained, using the $(2n+1)$ and $(2n+2)$ rules. Analysis of section V.4 shows that there are a lot of common terms appearing between the response equations of different Fock-space sectors, and also of different orders. It should be emphasized that this only results in computational advantage in terms of efficient reuse of certain computer programs, not in the sense of reuse of quantities such as $\overline{H}$. Our results indicate that, given the existence of such common terms, calculations of higher-order properties using valence-universal MRCC up to [1,1] sector may be feasible. The diagrammatic equations for zeroth-order Lagrange multiplier presented in section V.4.2 will serve as a starting point in this direction.

The developments of this chapter enable introduction of efficient property and gradient computations for the VUMRCC theory, opening the route for investigation of excited state potential energy surfaces using size-extensive theories. This is especially relevant for the [1,1] sector for which it is known that valence-universal MRCC is the only fully size-extensive theory available.

References

1. (a) T. H. Schucan and H. A. Weidenmuller, Ann. Phys. (N.Y.) **73**, 108 (1972) (b) ibid. **76**, 483 (1973)

2. P. J. Ellis and E. Osnes, Rev. Mod. Phys. **49**, 777 (1977)

3. D. Mukherjee and S. Pal, Adv. Quant. Chem. **20**, 292 (1989)
4. (a) G. Hose and U. Kaldor, J. Phys. **B12**, 3827 (1979) (b) ibid. Phys. Scripta. **21**, 357 (1980) (c) ibid. Chem. Phys. **62**, 419 (1981) (d) ibid. J. Phys. Chem. **86**, 2133 (1982)
5. B. Jezioroski and H. J. Monkhorst, Phys. Rev. **A24**, 1968 (1982)
6. B. H. Brandow, in *New Horizons in Quantum Chemistry*, edited by P. O. Lowdin and B. Pullman, (Riedel, Dordrecht, 1983)
7. (a) I. Lindgren, Phys. Scripta **32**, 291 (1985) (b) ibid, **32**, 611 (1985)
8. M. A. Haque and D. Mukherjee, Pramana **23**, 651 (1984)
9. D. Mukherjee, Proc. Ind. Acad. Sci. **96**, 145 (1986)
10. D. Mukherjee, Chem. Phys. Lett. **125**, 207 (1986)
11. D. Mukherjee, Int. J. Quant. Chem. **S20**, 409 (1986)
12. I. Lindgren and D. Mukherjee, Phys. Rep. **151**, 93 (1987)
13. W. Kutzelnigg, in *Aspects of many-body effects in molecules and extended systems, Lecture notes in Chemistry,* edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p35
14. (a) W. Kutzelnigg, D. Mukherjee, and H. Koch, J. Chem. Phys. **87**, 5902 (1987) (b) D. Mukherjee, W. Kutzelnigg, and H. Koch, J. Chem. Phys. **87**, 5911 (1987) (c) S. Koch and D. Mukherjee, Chem. Phys. Lett. **145**, 321 (1988)
15. D. Sinha, S. Mukhopadhyay, and D. Mukherjee, Chem. Phys. Lett. **129**, 369 (1986)
16. (a) L. Meissner, S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **91**, 6187 (1989) (b) L. Meissner and R. J. Bartlett, J. Chem. Phys. **92**, 561 (1990)
17. A. Balkova, S. A. Kucharski, L. Meissner, and R. J. Bartlett, J. Chem. Phys. **95**, 4311 (1991)

18. (a) S. Berkovic and U. Kaldor, Chem. Phys. Lett. **199**, 42 (1992) (b) S. Berkovic and U. Kaldor, J. Chem. Phys. **98**, 3090 (1993)
19. (a) R. Mattie, M. Rittby, R. J. Bartlett, and S. Pal, in *Aspects of many-body effects in molecules and extended systems, Lecture notes in Chemistry,* edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p143 (b) U. Kaldor, in same volume, p154
20. S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, J. Chem. Phys. **88**, 4357 (1988)
21. (a) M. A. Haque and U. Kaldor, Chem. Phys. Lett. **117**, 347 (1985) (b) ibid, **120**, 261 (1985)
22. (a) S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, Chem. Phys. Lett. **137**, 273 (1987) (b) N. Vaval, S. Pal, and D. Mukherjee, Theor. Chem. Acc. **99**, 100 (1998) (c) N. Vaval and S. Pal, J. Chem. Phys. **111**, 4051 (1999)
23. S. R. Hughes and U. Kaldor, Phys. Rev. A **47**, 4705 (1993)
24. (a) S. Pal, Phys. Rev. **A39**, 39 (1989) (b) S. Pal, Int. J. Quant. Chem. **41**, 443 (1992)
25. (a) D. Ajitha, N. Vaval, and S. Pal, J. Chem. Phys. **110**, 2316 (1999) (b) D. Ajitha and S. Pal, Chem. Phys. Lett. **309**, 457 (1999) (c) D. Ajitha and S. Pal , J. Chem. Phys. **114**, 3380 (2001) (d) N. Vaval and S. Pal, Chem. Phys. Lett. **300**, 125 (1999)
26. P. G. Szalay, Int. J. Quantum Chem. **55**, 151 (1995)
27. M. A. Haque and D. Mukherjee, J. Chem. Phys. **80**, 5058 (1984)
28. (a) T. Helgaker and P. Jorgensen, Theor. Chim. Acta. **75**, 111 (1989) (b) H. Koch, H. J. A. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria, H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990)
29. L. Meissner, J. Chem. Phys. **103**, 8014 (1995)

30. (a) L. Meissner, and M. Nooijen, J. Chem. Phys. **102**, 9604 (1995) (b) M. Nooijen, J. Chem. Phys. **104**, 2638 (1996)
31. L. Z. Stolarczyk and H. J. Monkhorst, Phys. Rev. A **32**, 725 (1986)
32. H. J. Monkhorst, Int. J. Quantum Chem. **S11**, 421 (1977)
33. R. J. Bartlett, in *Geometrical Derivatives of Energy Surface and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht,1986), p35
34. E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989)
35. D. Ajitha and S. Pal, J. Chem. Phys. **111**, 3832 (1999); **111**, 9892(E) (1999)
36. (a) D. Mukherjee and P. K. Mukherjee, Chem. Phys. **37**, 325 (1979) (b) Ghosh, D. Mukherjee, and S. N. Bhattacharya, Mol. Phys. **43**, 173 (1981) (c) S. Ghosh and D. Mukherjee, Proc. Ind. Acad. Sci. Chem. Sci. **93**, 947 (1984)
37. J. E. Rice and R. D. Amos, Chem. Phys. Lett. **122**, 585 (1985)
38. C. Dykstra, P. Jassien, Chem. Phys. Lett. **109**, 388 (1984)

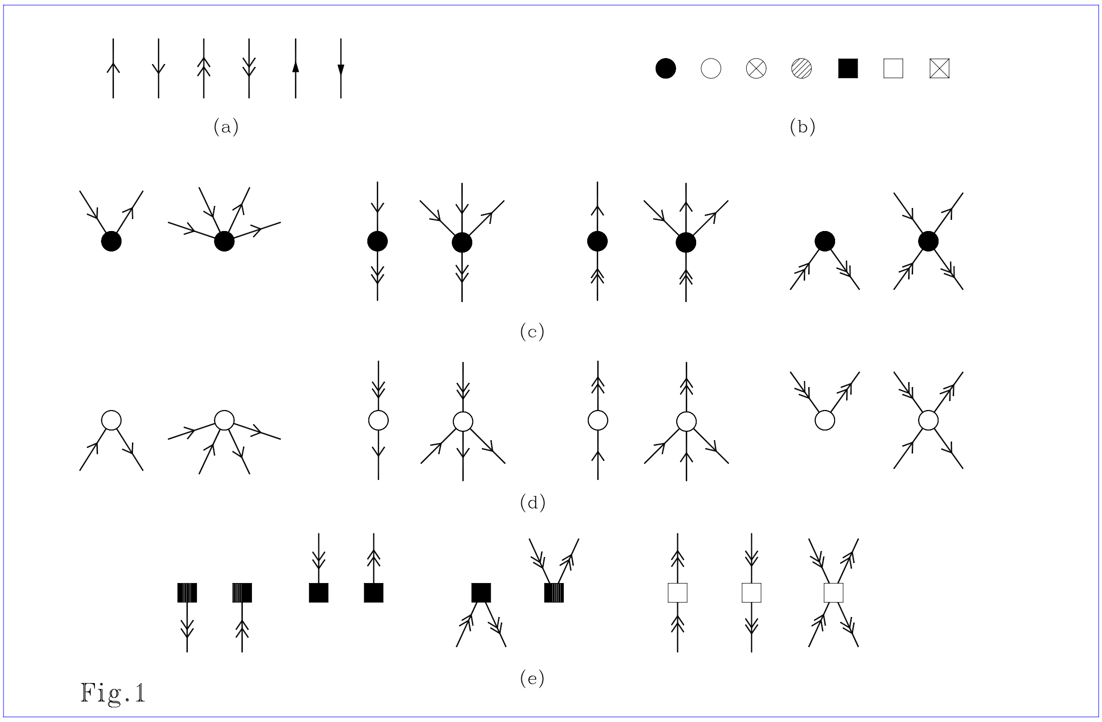

Fig.V.1: (a) Lines with single and double arrows respectively represent both active and inactive holes or particles, and only active holes and particles. Lines with filled thick dark arrows (dummy lines) also represent active holes or particles. Presence of a pair of such incoming and outgoing hole or particle dummy lines means summation over their orbital labels as explained in section V.4.2. (b) Different types vertices: filled and open circles represent a cluster amplitude T-vertex and Lagrangian multiplier Λ-vertex respectively. A circle with two-crossed lines represent Hamiltonian H, circle with filled oblique lines represent $\overline{H}$ as explained in section V.4.2. The three squares represent model-space coefficients $\tilde{C}_A$ and C_A, effective Hamiltonian H_{eff} and generic vertices respectively as explained in section V.4.2. (c)-(d) Structure of one and two-body parts of T and Λ vertices for various sectors. (e) Structure of model space coefficient and effective Hamiltonian vertices for various sectors.

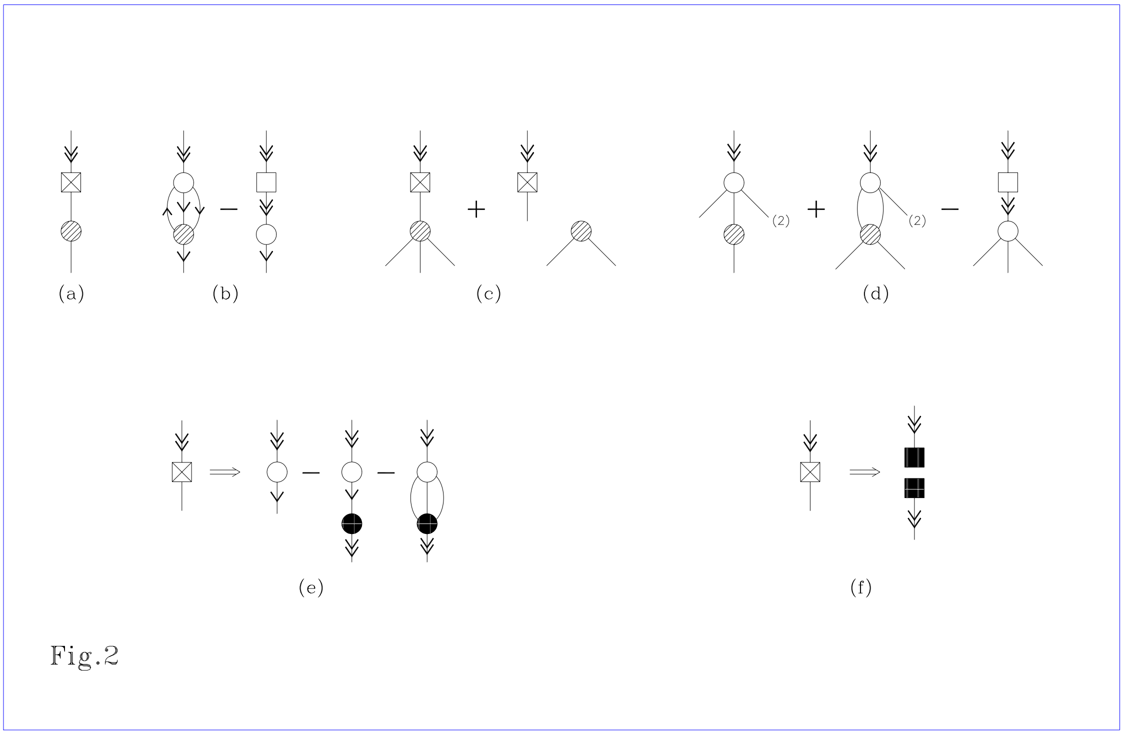

Fig.V.2: Diagram templates for homogenous terms of [0,1] sector. (a) and (b) represent one-body terms, (c) and (d) represent two-body terms. (e) is generic vertex which has to be inserted into (a) and (c). Some inhomogeneous terms can also be generated using generic vertex in (f) as explained in section V.4.2

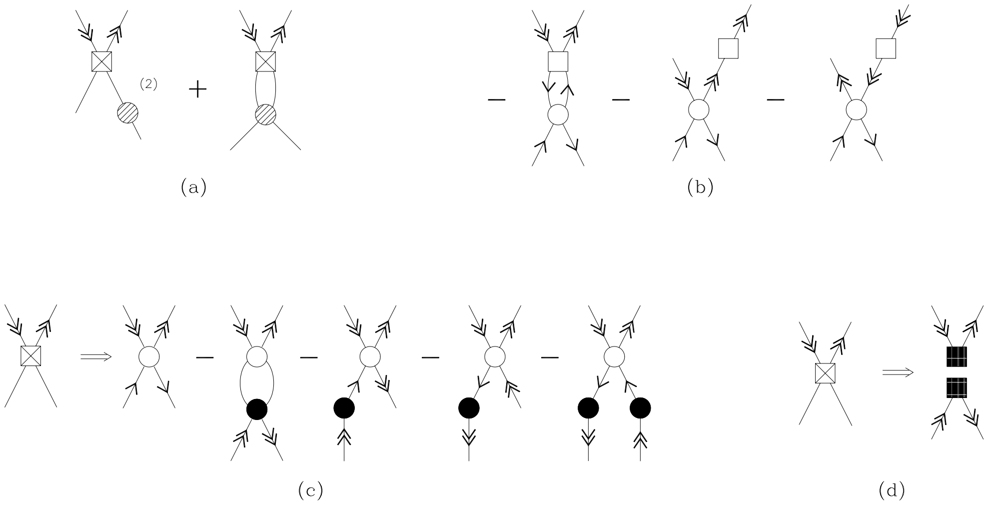

Fig.3

Fig.V.3: Diagram templates for homogenous terms of [1,1] sector. (a) and (b) represent two-body terms, (c) is generic vertex which has to be inserted into (a). Some inhomogeneous terms can also be generated using generic vertex in (d) as explained in section V.4.2

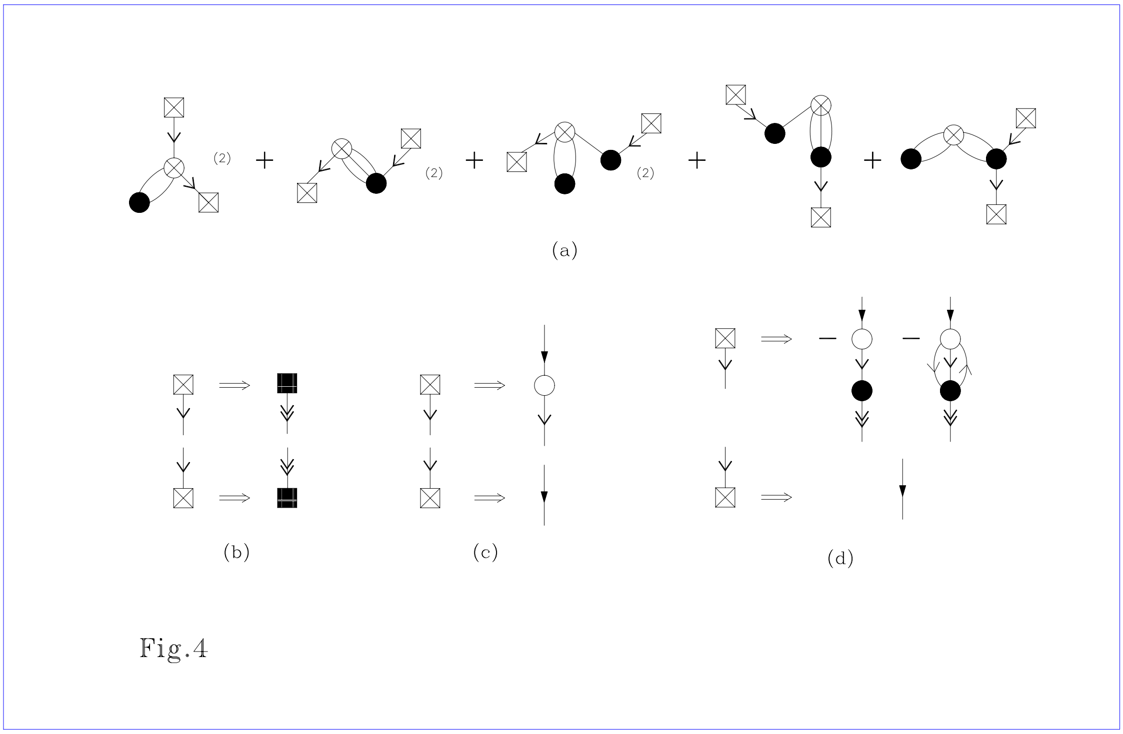

Fig.V.4: Diagram templates to describe influence of [0,1] sector effective Hamiltonian and one-body equations on [0,0] sector. $\bar{H}$ has been expanded and diagrams have been drawn in terms of $T^{[0,0]}$-vertex. Insertion of generic vertices in (b)-(d) into templates in (a) generate different first and second group of inhomogeneous terms as explained in section V.4.2. Required open diagrams can be obtained after these insertions by systematically deleting a $T^{[0,0]}$-vertex in all possible ways.

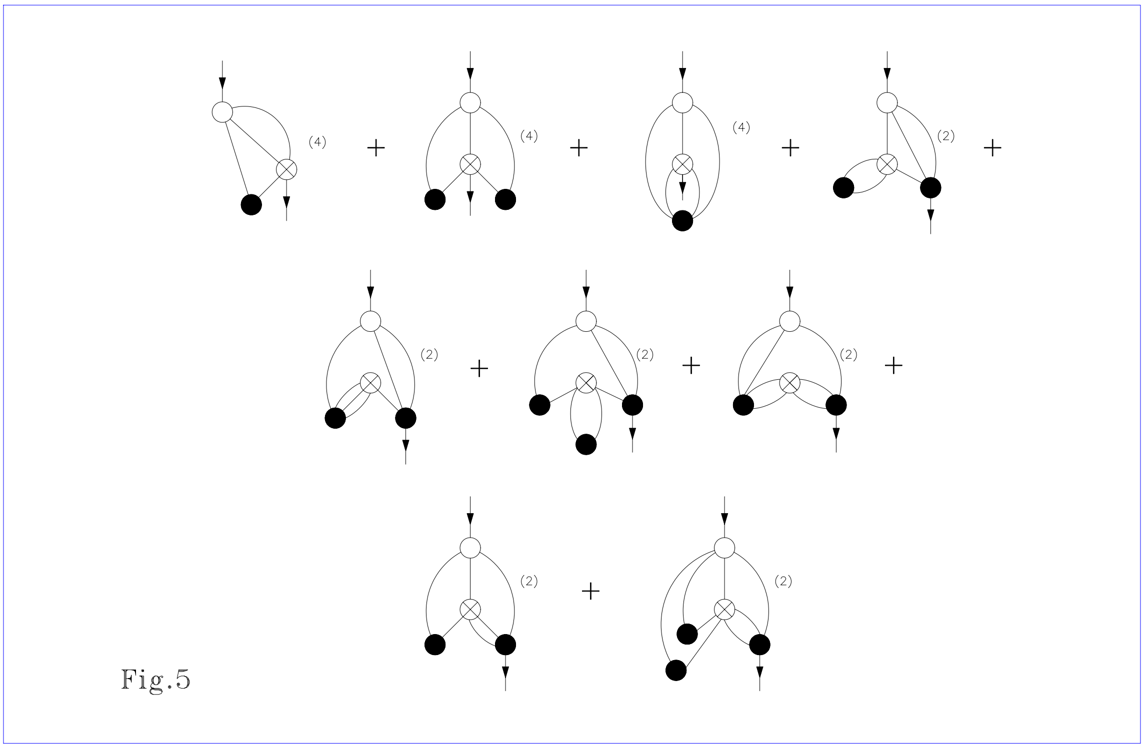

Fig.V.5: Diagram templates to describe influence of [0,1] sector effective Hamiltonian and two-body equations on [0,0] sector. $\bar{H}$ has been expanded and diagrams have been drawn in terms of $T^{[0,0]}$-vertex. Required open diagrams can be obtained by systematically deleting a $T^{[0,0]}$-vertex in all possible ways.

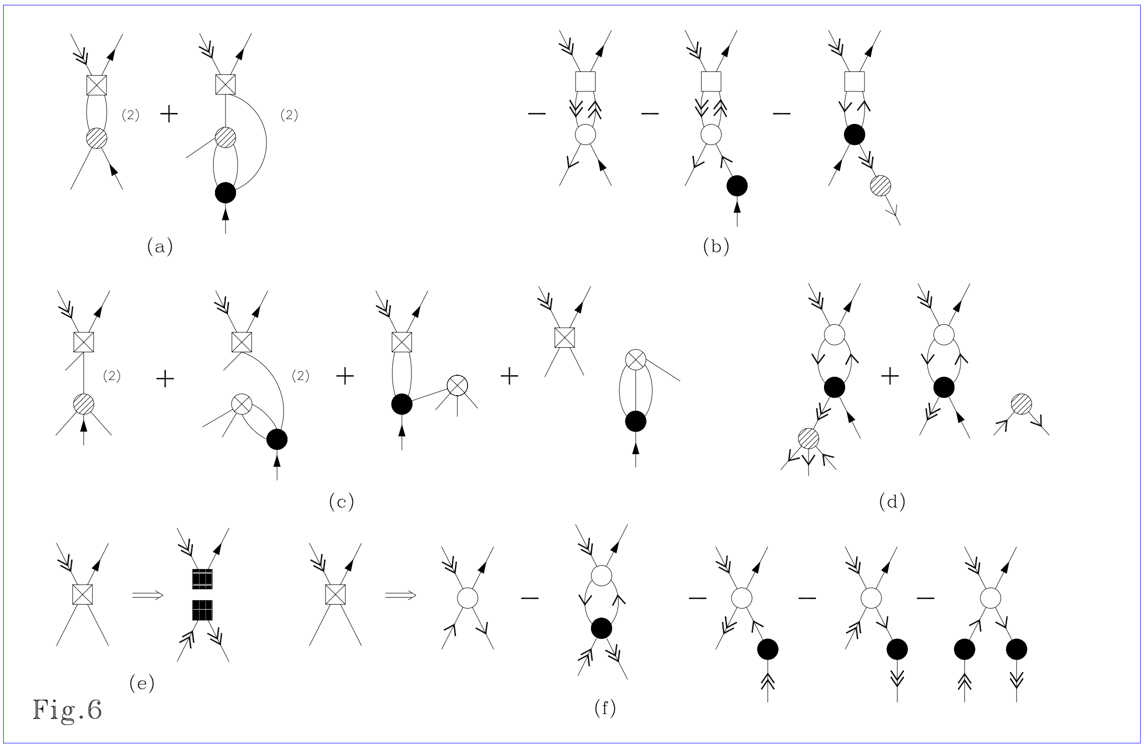

Fig.V.6: Open diagram templates to describe influence of [1,1] sector effective Hamiltonian and two-body equations on [0,1] sector. The [1,1] sector equations are obtained by hole-particle reversal. (a)-(b) represent one-body equations and (c)-(d) represent two-body equations. Different inhomogeneous terms can be generated using insertion of generic vertices in (e)-(f) into (a) and (c) as explained in section V.4.2.

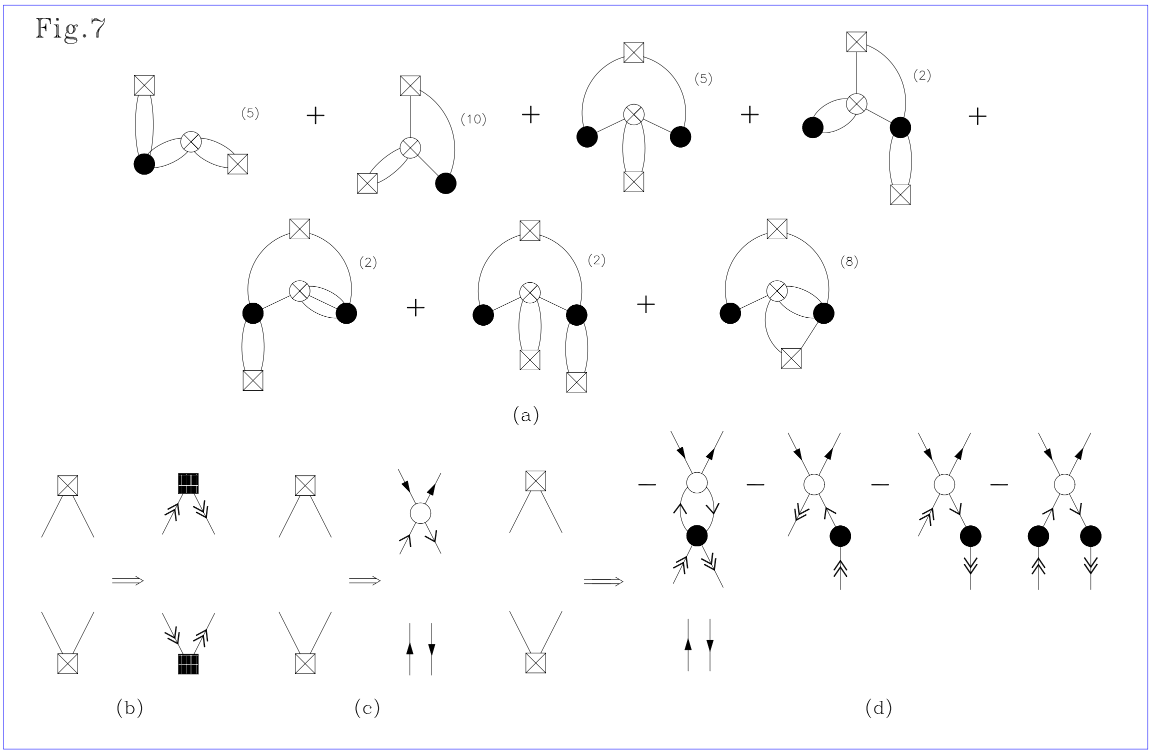

Fig.V.7: Diagram templates to describe influence of [1,1] sector effective Hamiltonian and two-body equations on [0,0] sector. $\bar{H}$ has been expanded and diagrams have been drawn in terms of $T^{[0,0]}$-vertex. Required open diagrams can be obtained by systematically deleting a $T^{[0,0]}$-vertex in all possible ways.

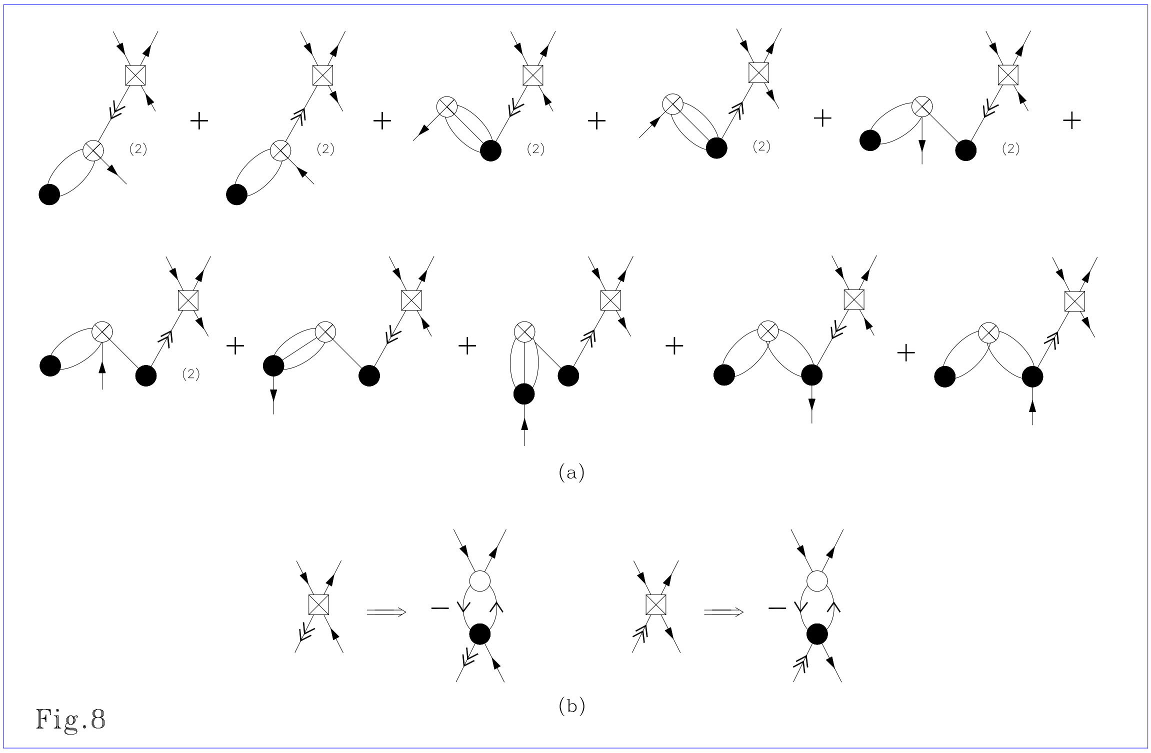

Fig.V.8: Diagram templates to describe influence of [1,1] sector $\overline{\Omega H}_{eff}^{[0,1]}$ and $\overline{\Omega H}_{eff}^{[1,0]}$ terms on [0,0] sector.

Chapter VI

Attempts towards formulation of a size-extensive stationary state-selective MRCC theory

VI.1 Introduction

So far, we have viewed constrained variation approach (CVA)[1-2] only as a method to generalize the Z-vector method[3-5] for higher-order properties. It is not necessary to construct Lagrange multipliers or Z-vector if only energy is to be computed. These are just some additional parameters which are required when energy derivatives are needed. In other words, Lagrange multipliers or Z-vector are not accorded any status as parameters of the underlying theory itself, .i.e., as parameters of electronic wavefunction. This view point is all right if one is only interested in obtaining energy derivatives of a theory formulated in a non-variational framework.

However, there is an alternative view point in which CVA is viewed as a way to construct a stationary reformulation of the underlying theory. The fact that zeroth-order Lagrange multipliers are treated in the same way as other zeroth-order quantities of the theory shows that they may be accorded some status as natural parameters of the theory. Due to their linear appearance in the functional, they are decoupled from other parameters. It is well-known that, this alternative view point, in context of SRCC, directly leads to extended coupled-cluster (ECC) theory developed by Arponen.[6-8] In fact, Arponen[6,8] proposes an energy functional containing de-excitation amplitudes in a linear fashion. These de-excitation amplitudes can be identified to be same as Z-vector of Bartlett and coworkers[4-5] and the Lagrange multipliers used by Jorgensen and coworkers.[2c] Therefore, Arponen's linear energy functional is essentially the same as

SRCC constrained variation functional of Jorgensen and coworkers.[2c] By a suitable exponential parameterization of linear de-excitation operator in terms of a de-excitation cluster operator, energy functional used in ECC theory can be easily constructed.

Similarly, it is natural to think that constrained variational approach for MRCC, as formulated in third and fifth chapter, may give some clues on how to generalize ECC for multi-reference cases. The state-dependent nature of constrained variational functional immediately indicates that, in an MR-ECC theory, the excitation and de-excitation cluster-amplitudes are coupled to model space coefficients. Such a picture is closer to recent state-selective MRCC theories[9] than to effective Hamiltonian MRCC theories.

State-selective or single-root theories have long been perceived as attractive alternatives to multi-root theories. Such theories are considered to be useful for description of molecular potential energy surface over a wide-range of geometries, without getting into convergence difficulties often associated with multi-root theories. Several such theories have appeared in recent times.[9]

In this chapter, we describe our attempts towards formulating a stationary size-extensive state-selective MRCC theory which generalizes single-reference ECC to multi-reference cases. At the outset, we should mention that such attempts have been rather unsuccessful in the sense that we have not quite been able to obtain a consistent size-extensive MR-ECC functional which, upon stationarity, leads to electronic Schrödinger equation. We identify a possible paradigm within which a possible MR-ECC formulation can be searched. Based on CVA for SUMRCC theory and for a non-stationary state-selective MRCC theory recently proposed by Mukherjee and coworkers,[9-11] two stationary state-selective MRCC theories are derived. The structure of these theories are discussed by analyzing their working equations. We outline possible theoretical problems which need to be solved to reach a solution within the proposed paradigm.

VI.2 Stationary single-reference coupled-cluster theories

Stationary (or variational) approaches are based on the general Euler-Lagrange variation principle.[12] Its application to quantum mechanics leads to variational principle.[13] This states that wave-function Ψ which makes the energy functional $\langle \Psi | \hat{H} | \Psi \rangle$ stationary with respect to small variations in Ψ, subject to normalization condition $\langle \Psi | \Psi \rangle = 1$, is a solutions of Schrödinger equation and vice-versa.

$$\delta\Big[\langle \Psi | \hat{H} | \Psi \rangle - E\big(\langle \Psi | \Psi \rangle - 1\big)\Big] = 0 \quad \Leftrightarrow \quad \hat{H} | \Psi \rangle = E | \Psi \rangle \tag{6.1}$$

Here, E is the Lagrange multiplier associated with normalization condition, and will be recognized as energy or eigenvalue of Schrödinger equation. By appropriately parameterizing Ψ to cover entire Hilbert-space or a portion thereof, and making the energy functional stationary with respect to variations in these parameters, Schrödinger equation can be solved.[13] As discussed in the first chapter, in context of electronic Schrödinger equation, Ψ can be linearly parameterized in terms of Slater determinants. This leads to configuration interaction method of diagonalisation of Hamiltonian matrix over the linear vector space spanned by of Slater determinants.

Realization of exponential coupled-cluster ansatz $\Psi = e^{T} | \Phi_0 \rangle$ for many-electron systems opened up new avenues based on the use of variational principle. The variational coupled-cluster (VCC) method is based the following energy functional.[14]

$$E = \frac{\langle \Phi_0 | e^{T^\dagger} \hat{H} e^{T} | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^{T} | \Phi_0 \rangle} \tag{6.2}$$

This functional is also referred to as XCC (expectation value coupled-cluster) as it is the expectation value of Hamiltonian.[15-19] Here, $T^{\dagger}$ is adjoint of cluster operator T. While cluster operator T induces excitations, $T^{\dagger}$ operator induces de-excitations. Applying variation principle to the above functional with respect to all variations in T and $T^{\dagger}$ leads to their defining equations. Since the functional is hermitian, equations defining $T^{\dagger}$ are adjoint of equations defining T, and only one set of them needs to solved.

However, it is not possible to carry out such a variation procedure in practice. This is because both the numerator and denominators are infinite series in T and $T^{\dagger}$. Furthermore, this energy functional does not explicitly exhibit the connected nature of energy as it happens in MBPT or the standard SRCC theory. It has been shown that a manifestly connected form for energy functional can be obtained by expanding the numerator and the denominator using generalized Wick's theorem.[14,17-18] The numerator can be shown to be product of a connected term and the denominator.[17] Therefore, the denominator cancels out leaving the following explicitly connected energy functional.

$$E = \langle \Phi_0 | e^{T^{\dagger}} \hat{H} e^{T} | \Phi_0 \rangle_{conn} \tag{6.3}$$

This functional is now in a suitable form for carrying out variation. By a suitable low rank (usually doubles or singles and doubles) truncation of cluster operators, variational equations for cluster-amplitudes may be set up. However, despite truncation of cluster operators, even this functional is a non-terminating series, and its full variation is not possible. Suitable truncation of the functional itself is needed for practical applications. Various truncations have been studied in literature. Pal and coworkers[17-20] have used algebraic or polynomial truncation based on the maximum number different cluster operators retained in the functional. Quadratic as well cubic truncation schemes have been employed.[20] On the other hand, Bartlett and coworkers have used truncation by retaining terms whose initial perturbative contributions appear up to a given order n, and resultant approximation is referred to as XCC(n).[16a,21]

Alternatively, Kutzelnigg and coworkers[15] have proposed the use of an unitary exponential ansatz for the wavefunction as follows.

$$|\Psi\rangle = U\,|\Phi\rangle = e^{\sigma}\,|\Phi\rangle \qquad \sigma = -\sigma^{\dagger} \tag{6.4}$$

The unitary wave-operator U is written as exponential of an anti-hermitian operator σ. Use of ansatz Eq (6.4) in the expectation value of Hamiltonian leads to the following unitary coupled-cluster (UCC) functional.

$$E = \langle \Phi_0 \,|\, e^{-\sigma}\hat{H}e^{\sigma} \,|\, \Phi_0 \rangle \tag{6.5}$$

For UCC functional, there is no denominator. The denominator can be shown to be equal to unity, because of unitary property of the wave-operator. However, even this functional, although connected due to Baker-Campbell-Hausdorf (BCH) formula for $e^{-\sigma}\hat{H}e^{\sigma}$, can be shown to be an infinite series. Both variational and non-variational schemes for calculation of σ can be envisaged. However, truncation of series for $e^{-\sigma}\hat{H}e^{\sigma}$ is needed in both schemes. Pal and coworkers,[17] realizing σ as $T - T^{\dagger}$, have shown that variational scheme with UCC functional Eq (6.5) is identical to variational scheme with connected form of XCC functional Eq (6.3).

It is well known that energy obtained in variational theories posses an upper-bound property. For variational theories based on coupled-cluster ansatz, it has been shown that there is a loss of this upper-bound property in practical applications with terminated functionals.[18] This is not a serious drawback however, given that, even standard SRCC energy does not have upper-bound property. Upper-bound property is no longer considered to be as important as it used to be in earlier days of quantum chemistry. Interest in variational theories is primarily due to ease in property evaluation resulting from generalized Hellmann-Feynman theorem and $(2n+1)$ rules satisfied by such theories.[13]

Another serious drawback of variational theories was recognized when their applications were initiated in quantum chemistry.[19-22] Although energy functional is explicitly connected, the variation procedure, namely differentiation of energy functional with respect to cluster-amplitudes, leads to disconnected terms in equations for cluster-amplitudes. It was realized that, due to non-linear nature of energy functional, such disconnected terms eventually lead to energies which are not size-extensive. It was shown that only for certain kind of truncations of functional, namely the truncations used by Bartlett and coworkers,[16a,21] these disconnected terms cancel among themselves giving size-extensive energy. This seriously limits their use in quantum chemistry.

A stationary coupled-cluster formulation which leads to size-extensive energies was proposed by Arponen[6] who referred it as extended coupled-cluster (ECC) method. ECC energy functional can be derived from the following bivariational form of exact energy functional.

$$E = \frac{\langle \Phi_0 | e^S \hat{H} e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^S e^T | \Phi_0 \rangle} \tag{6.6}$$

Here, S is a de-excitation operator similar in structure to $T^\dagger$. From the bivariation principle, it is known that, making this functional stationary with respect to variations in S and T leads to right-hand and left-hand side Schrödinger equations respectively.

Using denominator cancellation methods, it can be shown that this functional can be written as follows.

$$E = \frac{\langle \Psi' | \hat{H} | \Psi \rangle}{\langle \Psi' | \Psi \rangle} \tag{6.7}$$

$$| \Psi \rangle = e^{T} | \Phi_0 \rangle \tag{6.8}$$

$$\langle \Psi' | \ = \langle \Phi_0 | \left(1 + \Lambda\right) e^{-T} \tag{6.9}$$

$$\langle \Psi' | \Psi \rangle = 1 \tag{6.10}$$

Here, Λ is a de-excitation operator similar in structure to S. Functional (6.7) is a unsymmetrical expectation value functional between left and right states, $\langle \Psi' |$ and $| \Psi \rangle$. Biorthonormal condition Eq (6.10) between these two states can be used to write the functional as follows.

$$E = \langle \Phi | \left(1 + \Lambda\right) e^{-T} \hat{H} e^{T} | \Phi \rangle \tag{6.11}$$

As proposed by Arponen,[6] by considering Λ and T as independent parameters for variation and making the above functional stationary with respect these parameters, we get the standard SRCC equations along with corresponding Z-vector method. In fact, Eq (6.11) is just the SRCC constrained variation functional discussed in the second chapter. By exponentially parameterizing $\left(1 + \Lambda\right)$ in Eq (6.11) as $\langle \Phi_0 | \left(1 + \Lambda\right) = \langle \Phi | e^{\tilde{\Sigma}}$ leads to following functional.

$$E = \langle \Phi_0 | e^{\tilde{\Sigma}} e^{-T} \hat{H} e^{T} | \Phi_0 \rangle = \langle \Phi_0 | e^{\tilde{\Sigma}} e^{-T} \hat{H} e^{T} e^{-\tilde{\Sigma}} | \Phi_0 \rangle \tag{6.12}$$

This is just the vacuum expectation value of a double similarity transformed Hamiltonian $e^{\tilde{\Sigma}} e^{-T} \hat{H} e^{T} e^{-\tilde{\Sigma}}$. This is a terminating functional, although termination depends on rank of cluster operators. It has been known that double similarity transformation represents a general form of similarity transformation of Hamiltonian.[23] However, it is not necessary for obtaining of energies which can be done with a single similarity transformation as in SRCC.

As Arponen shows, a variation procedure can be setup with ECC energy functional Eq (6.12). Such a procedure suffers from same size-extensivity problems of XCC methods as discussed earlier. However, it is possible to convert Eq (6.12) into an equivalent functional form which, upon variation, leads to connected equations and size-extensive energies. As demonstrated by Arponen,[6,8] this can be achieved by a change of variables from $\left(\tilde{\Sigma},T\right)$ to $\left(\tilde{\Sigma},\tilde{T}\right)$. All the de-excitations in Eq (6.12) which are not connected to Hamiltonian, and fully contracted by a single T operator, are absorbed into T to define a new independent variable $\tilde{T}$. In terms of new variables, the functional is written as,

$$E=\langle\Phi_0\,|\,e^{\tilde{\Sigma}}e^{-\tilde{T}}\hat{H}e^{\tilde{T}}e^{-\tilde{\Sigma}}\,|\,\Phi_0\rangle_{DL} \tag{6.13}$$

This is the ECC energy functional as proposed by Arponen.[6,8] Here, the subscript DL means that only double linked terms are retained in the functional. Double linking means that while each $\tilde{T}$ is linked Hamiltonian, each $\tilde{\Sigma}$ is either connected to Hamiltonian vertex or else to two distinct $\tilde{T}$ vertices. While double similarity transformation ensures terminating nature of the functional, double linking property ensures that a variational method based on energy functional Eq (6.13) leads to connected equations and size-extensive energies.

Despite energy being size-extensive, ECC functional seems to be not useful for computation of energies. This is because, it contains double the number of coupled parameters as compared to standard SRCC, and hence is computationally expensive. The advantages of using ECC functional were highlighted by Pal,[24] who advocated its use for molecular properties. The inclusion of double number of parameters is compensated by variational nature of equations which leads to simplifications for molecular properties. In fact, even in standard SRCC theory, two sets of parameters are required for property computation, namely the cluster-amplitudes and the Z-vector. In SRCC, calculation of cluster-amplitudes are decoupled from Z-vector calculations. In ECC, these two sets of parameters are included right from the beginning and hence they become coupled. Fortunately, again, this coupling does not go uncompensated for. It is known that ECC sums a larger class of perturbation diagrams, and its energy is much more accurate than SRCC energy.[6-8] Since molecular properties are sensitive to accuracy of energy, molecular properties computed with ECC are expected to be more accurate than their SRCC counterparts. Pal and coworkers[22,24-25], Bartlett and coworkers,[16b,26] and Head-Gordon and coworkers[27] have extensively studied the efficacy of ECC method.

With the emergence of ECC as a size-extensive variational (or stationary) coupled-cluster theory useful for computation of energies and molecular properties, it is natural to look for its possible generalization to multi-reference cases. Since single-reference ECC is closely related to constrained variation approach for SRCC,[25b] one may try to formulate MR-ECC using the MRCC constrained variation approach discussed in the third chapter. Some general conclusions are straightforward to reach. It has been emphasized in the third chapter that MRCC constrained variation functional is state-dependent resulting in state-dependent Lagrange multipliers. Therefore, MR-ECC energy functional must also be state-dependent. In effective Hamiltonian MRCC theories, the cluster-operators are state-independent. After exponential parameterization of Lagrange multipliers to define suitable de-excitation amplitudes, variation (or stationarity) of resulting functional leads to coupling of original cluster-amplitudes with the new de-excitation amplitudes. This clearly indicates that, in MR-ECC method, cluster amplitudes and de-excitation amplitudes will both have to be state-dependent, and intrinsically coupled to model space coefficients.

Therefore, it is clear that MR-ECC is a kind of stationary theory where its parameters are specific to a particular state among the quasi-degenerate manifold. In fact, this picture of MR-ECC is more closer to state-selective or single-root theories which are recently being pursued.[9] In the next section, we briefly discuss these theories and identify their basic features.

VI.3 Basic features of state-selective or single-root theories

One basic theme that has been important in development of effective Hamiltonian multi-reference theories is the separation of dynamical and non-dynamical electron correlation.[28] While dynamical correlation refers to the weak interaction of quasi-degenerate states with states in complementary space, non-dynamical correlation refers to the rather strong interaction of quasi-degenerate states among themselves. If states in complementary space are well separated in energy from quasi-degenerate states, dynamical correlation effects work out to be approximately similar for all the quasi-degenerate states. This physical idea is translated into mathematical statement that wave-operator describing dynamical correlation is same for all quasi-degenerate states in the manifold. This leads to construction of an effective Hamiltonian which is again same for all states in the manifold.

The idea that parameters describing dynamical electron correlations are same for quasi-degenerate states well-separated from the rest of the states has played very important role in development of multi-reference theories.[28] This is particularly evident in valence-universal approaches where information about dynamical correlation in lower-valence systems are used as input to calculate additional dynamical correlation effects in higher-valence systems.

This, to some extent, explains the success of these approaches for spectroscopic quantities where states differ by a few electrons (typically one or two electrons). However, for potential energy surfaces, such a reasoning has somehow not been so successful. The reason probably is that the separation between dynamical and non-dynamical correlation, and dynamical part being similar for different states, does not seem to be a sufficiently accurate picture over a wide-range of geometries. As one moves from one region of potential energy surface to another region, the nature of states changes significantly. Therefore, each state has to have its own optimal set of parameters to describe correlation effects. For example, it known that different states require different set of orbitals for optimal description.

State-selective or one-state approaches are essentially based on this idea. In such theories, although wavefunction parameterization is same for different quasi-degenerate states, the parameters are evaluated so as to be optimal for a specific state, subject to limitations of parameterization. It has been generally appreciated that state-selective theories are more suitable for description of potential surfaces over a range of geometries.

Different state-selective theories based on different ideas for wave-operator ansatz have been proposed throughout these years. Notable among them are the ones by Silverstone and Sinanoglu,[29] Harris,[30] Paldus and coworkers,[31] Nakatsuji and Hirao,[32] Banerjee and Simons,[33] Baker and Robb,[34] Laidig and Bartlett,[35] Taneka and Terashima,[36] Hoffman and Simons,[37] Adamowicz and coworkers,[38] Szalay and coworkers,[39] Malrieu and coworkers,[40] Mukherjee and coworkers,[9-11,41] Masik and Hubac,[42] and Nooijen.[43] Silverstone and Sinanoglu were the first to propose a state-selective MRCC theory. Earlier generation theories often suffered from many theoretical problems such as the incompleteness of the wave-operator to recover full-CI limit, lack of general applicability, appearance of redundant cluster operators which can not be determined from the knowledge of considered state alone. Recently, such problems have been resolved to some extent and several fully or approximately size-extensive state-selective MRCC formulations have been proposed by Malrieu and coworkers,[40] Masik and Hubac,[42] and Mukherjee and coworkers.[9-11,41]

A major theoretical difficulty which prevents straightforward formulation a state-selective MRCC approach is the redundancy or linear dependence among cluster operators. This issue has been extensively discussed in a by Mukherjee and coworkers who also present a brief survey of previous state-selective and intermediate Hamiltonian approaches.[9] They also emphasize two paradigms for state-selective theories where this redundancy problem is solved in different ways. In the first paradigm , referred to by them as decontracted or relaxed coefficients description, a physically motivated additional sufficiency conditions are postulated to resolve redundancy. The cluster-amplitudes and model space coefficients are coupled to each other, and are iteratively updated to their corresponding values in the exact wavefunction. In the second paradigm, referred to as contracted or unrelaxed coefficients description, cluster expansion with respect to entire multi-reference wavefunction is carried out. Redundancy is eliminated by retaining only the linearly independent cluster-amplitudes in the cluster operators. Here, model space coefficients are held fixed (unrelaxed) while cluster-amplitudes are being determined.

Mukherjee and coworkers have proposed state-selective MRCC theories within both these paradigms. Based on the assumption of a dominant single determinant and single-reference exponential ansatz for the wave-operator and resolving redundancy conditions by separability assumption on dynamical and non-dynamical correlation, they have obtained a size-extensive state-selective MRCC theory conforming to the decontracted description.[41] Later on, without assuming a single dominant determinant and based on the Jezioroski-Monkhorst ansatz, they have been able to postulate general size-extensive state-selective MRCC theory again conforming to decontracted description.[9-11] This approach is conceptually simple and straight forward. In both these descriptions, the energy and model space coefficients are determined from an eigenvalue equation of an intermediate Hamiltonian operator which depends on cluster amplitudes. These, in turn, depend on model space coefficients through the sufficiency conditions. Therefore, the parameters describing dynamical and non-dynamical correlation are coupled and lead to optimal values for both of them. Mukherjee and coworkers[9] have also formulated a state-selective MRCC approach conforming to the contracted description. This is done by introducing concept of extended normal ordering and analogue of Wick's theorem with entire multi-reference wavefunction treated as a vacuum.[44-45] This contracted state-selective MRCC theory may be viewed as appropriate generalization of single-state MRPT approaches using internally contracted configurations as discussed in the first chapter.

VI.4 Stationary state-selective MRCC theories

In this section, we discuss stationary state-selective MRCC theories obtained by appropriate exponential parameterization of Lagrange multipliers in constrained variation functional. Two different functionals are used for this purpose. The first functional is the one used in third chapter, which corresponds to the state-universal MRCC theory. The second one corresponds to the state-selective MRCC theory recently formulated by Mukherjee and coworkers.[10-11]

The idea is to rewrite constrained variation functional as a bivariational energy functional corresponding to the eigenvalue problem for some kind of intermediate Hamiltonian defined over the model space. This intermediate Hamiltonian contains enough parameters (cluster amplitudes and de-excitation amplitudes) to permit consistent variation of the resulting functional. While variation with respect to (right and left) model space coefficients leads to (left and right) eigenvalue equation for intermediate Hamiltonian, variation with respect to cluster and de-excitation amplitudes results in their defining equations. These equations contain model space coefficients, and hence the resulting stationary state-selective MRCC theories conform to decontracted paradigm identified by Mukherjee and coworkers.[9]

VI.4.1 A stationary state-selective MRCC theory using constrained variation functional for state-universal MRCC

Consider the constrained variation functional for state-universal MRCC discussed in third chapter. Since model space coefficients are going to be coupled to cluster and de-excitation amplitudes, functional form proposed by Szalay,[46] Eq (3.10), is more suitable. Absorbing the second term into diagonal elements of the first term, it can be written as follows.

$$\mathcal{J}(\Theta)=\sum_{\mu,\nu}\tilde{C}_{I\nu}H_{int}^{\nu\mu}C_{\mu I}-E_I\left(\sum_{\mu}\tilde{C}_{\mu}^{I}C_{\mu}^{I}-1\right) \tag{6.14}$$

$$\begin{aligned} H_{int}^{\mu\mu} &= \langle\Phi_{\mu}|\left(1+\Lambda_{\mu}\right)e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \\ &\quad+\sum_{\lambda\neq\mu}\langle\Phi_{\mu}|\left(1+\Lambda_{\mu}\right)e^{-T_{\mu}}e^{T_{\lambda}}|\Phi_{\lambda}\rangle\langle\Phi_{\lambda}|e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \\ H_{int}^{\nu\mu} &= \langle\Phi_{\nu}|e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \quad \nu\neq\mu \end{aligned} \tag{6.15}$$

Here, H_{int} is some kind of intermediate Hamiltonian. With this, Eq (6.14) can be viewed as a bivariational energy functional corresponding to the eigenvalue problem for H_{int}. When Lagrange multipliers are determined by stationarity of this functional, H_{int} turns out to be same as state-universal MRCC effective Hamiltonian H_{eff}. By exponential parameterization of $1+\Lambda_{\mu}$ in terms of a new de-excitation operator S_{μ}, this intermediate Hamiltonian can be written as follows.

$$\begin{aligned} H_{int}^{\mu\mu} &= \langle\Phi_{\mu}|e^{S_{\mu}}e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \\ &\quad+\sum_{\lambda\neq\mu}\langle\Phi_{\mu}|e^{S_{\mu}}e^{-T_{\mu}}e^{T_{\lambda}}|\Phi_{\lambda}\rangle\langle\Phi_{\lambda}|e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \\ H_{int}^{\nu\mu} &= \langle\Phi_{\nu}|e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \quad \nu\neq\mu \end{aligned} \tag{6.16}$$

It may be noted that only diagonal elements of H_{int} have been altered. A stationary MRCC theory can be obtained by making this functional stationary with respect variations in all parameters. This procedure leads to following equations.

$$\begin{aligned} &\langle\Phi_{\mu}|\tau_q^{\dagger}(\mu)e^{S_{\mu}}e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle+ \\ &\sum_{\lambda\neq\mu}\langle\Phi_{\mu}|\tau_q^{\dagger}(\mu)e^{S_{\mu}}e^{-T_{\mu}}e^{T_{\lambda}}|\Phi_{\lambda}\rangle\langle\Phi_{\lambda}|e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \quad =0 \quad \forall\,\tau_q^{\dagger}(\mu) \end{aligned} \tag{6.17}$$

$$\begin{aligned} &\langle\Phi_{\mu}|e^{S_{\mu}}[e^{-T_{\mu}}\hat{H}e^{T_{\mu}},\tau_q(\mu)]|\Phi_{\mu}\rangle \\ &+\sum_{\lambda\neq\mu}\langle\Phi_{\mu}|e^{S_{\mu}}e^{-T_{\mu}}e^{T_{\lambda}}|\Phi_{\lambda}\rangle\langle\Phi_{\lambda}|[e^{-T_{\mu}}\hat{H}e^{T_{\mu}},\tau_q(\mu)]|\Phi_{\mu}\rangle \\ &-\sum_{\lambda\neq\mu}\langle\Phi_{\mu}|e^{S_{\mu}}e^{-T_{\mu}}\tau_q(\mu)e^{T_{\lambda}}|\Phi_{\lambda}\rangle\langle\Phi_{\lambda}|e^{-T_{\mu}}\hat{H}e^{T_{\mu}}|\Phi_{\mu}\rangle \qquad \forall\,\tau_q(\mu) \\ &+\sum_{\lambda\neq\mu}\frac{\tilde{C}_{I\lambda}C_{\lambda I}}{\tilde{C}_{I\mu}C_{\mu I}}\langle\Phi_{\lambda}|e^{S_{\lambda}}e^{-T_{\lambda}}\tau_q(\mu)e^{T_{\mu}}|\Phi_{\mu}\rangle\langle\Phi_{\mu}|e^{-T_{\lambda}}\hat{H}e^{T_{\lambda}}|\Phi_{\lambda}\rangle \quad =0 \end{aligned} \tag{6.18}$$

$$\sum_{\mu} H_{int}^{\nu\mu} C_{\mu I} = E_I C_{\nu I} \quad \forall \nu \tag{6.19}$$

$$\sum_{\nu} H_{int}^{\nu\mu} \tilde{C}_{I\nu} = E_I \tilde{C}_{I\mu} \quad \forall \mu \tag{6.20}$$

$$E_I = \sum \tilde{C}_{I\nu} H_{int}^{\nu\mu} \tilde{C}_{\mu I} \tag{6.21}$$

Here, it has been assumed that $\tilde{C}_{I\mu} C_{\mu I} \neq 0 \;\; \forall \mu$. While Eq (6.17)-(6.18) determine cluster and de-excitation amplitudes T_μ and S_μ, next three equations determine model space coefficients and energy via diagonalisation of H_{int}. From the above equations, it is clear that cluster and de-excitation amplitudes T_μ and S_μ are coupled to the model space coefficients through the last term in Eq (6.18) and will have be simultaneously solved in an iterative procedure. It is of interest to analyze the nature of this coupling. As in the state-universal MRCC, Eq (6.17) defining cluster operator T_μ for a given vacuum Φ_μ, couples it to the cluster operators $T_\lambda, \forall \lambda \neq \mu$ of all other vacuums. Here, T_μ is further coupled to de-excitation operator S_μ of the same vacuum. However, it is not directly coupled to de-excitation operators of other vacuums or to the model space coefficients. Indirect coupling with all other quantities enters through Eq (6.18), which defines de-excitation amplitude S_μ. In this equation, S_μ gets coupled to all other cluster operators, de-excitation operators, and the model space coefficients, mainly through the last term.

It is now clear that this procedure leads to a state-selective MRCC theory, in the sense that cluster and de-excitation operators defining dynamical correlation become state-dependent, as opposed to being state-independent in state-universal MRCC. Furthermore, this theory naturally conforms to the decontracted paradigm where cluster operators, de-excitation operators and model space coefficients are solved in an iterative procedure, relaxing them to occupy their optimal values in the final wavefunction.

When T_μ and S_μ are truncated to some low ranks, resulting H_{int} is not same as corresponding state-universal MRCC effective Hamiltonian H_{eff}. It should be noted that only one eigenvalue of H_{int} corresponds to energy of the required state, and the rest are extraneous. Only when T_μ and S_μ are not truncated, H_{int} becomes same as H_{eff} and all its roots become meaningful. As higher rank operators are included, H_{int} tends to become same as H_{eff}. Therefore, it may be surmised that extraneous roots of H_{int} are possibly some rough approximations to exact energies of other states. For this reason, we refer H_{int} as intermediate Hamiltonian.

VI.4.2 A stationary state-selective MRCC theory using constrained variation functional for state-selective MRCC of Mukherjee and coworkers

The state-selective MRCC proposed above may be thought of as one which tends towards being state-universal MRCC in the exact limit. Although it is not easy to prove, it is likely that coupling of cluster amplitudes with rest of the parameters progressively gets weaker and weaker as exact limit is approached, eventually vanishing in the exact limit. In other words, the state-selective MRCC theory derived above may be considered as one where coupling of cluster amplitudes with rest of variables is kept to a minimum. This is clear from the structure of intermediate Hamiltonian given in Eq (6.16) where coupling terms appear only in diagonal terms.

However, this feature is not necessary for a state-selective theory, i.e., it is not necessary for intermediate Hamiltonian to go over to corresponding effective Hamiltonian in the exact limit. Even in the exact limit, only one root of intermediate Hamiltonian may be meaningful. Moreover, it may be entirely possible to cook up some alternative H_{int} which goes over to H_{eff} in the exact limit, albeit in a different path.

Recently, Mukherjee and coworkers[10-11] have proposed a state-selective MRCC theory based on the Jezioroski-Monkhorst ansatz. Their approach does not involve the Bloch equation. Instead, they substitute the ansatz directly into Schrödinger equation for a specific state, and resolve the redundancy problem of cluster amplitudes by postulating some sufficiency conditions which do preserve size-extensivity, at the same time avoiding the intruder state problem. Their sufficiency conditions (which are nothing but equations to determine cluster amplitudes) couple the cluster amplitudes with the model space coefficients. Consequently, they are led to an approach where the model space coefficients and energies are obtained through the eigenvalue problem for an intermediate Hamiltonian resembling effective Hamiltonian of the state-universal MRCC theory.

Now, we formulate another stationary MRCC theory based on their state-selective theory. This is easily done by setting up a corresponding constrained variation functional, and going over to exponential parameterization of Lagrange multipliers. Multiplication of their cluster amplitude defining equation (15) in Ref.9 with $\tilde{C}_{I\mu}\lambda_I(\mu)$, with some manipulations leads to functional in Eq (6.14) with intermediate Hamiltonian defined as follows.

$$\begin{aligned} H_{int}^{\mu\mu} &= \langle \Phi_\mu | e^{S_\mu} e^{-T_\mu} \hat{H} e^{T_\mu} | \Phi_\mu \rangle \\ H_{int}^{\nu\mu} &= \langle \Phi_\nu | e^{S_\nu} e^{-T_\nu} e^{T_\mu} | \Phi_\nu \rangle \langle \Phi_\nu | e^{-T_\mu} \hat{H} e^{T_\mu} | \Phi_\mu \rangle \quad \nu \neq \mu \end{aligned} \tag{6.22}$$

This intermediate Hamiltonian is considerably different. In contrast to earlier one in Eq (6.16) where diagonal elements included all the coupling terms, here, diagonal term are very simple. All coupling terms containing product of exponentials have been moved to off-diagonal elements. Most notable feature is that, unlike earlier one where de-excitation operators were confined to diagonal terms of intermediate Hamiltonian, here they are present in each of the off-diagonal terms. Essentially, de-excitation operators have been distributed all over. To see effect of this feature, we derive equations for cluster and de-excitation amplitudes.

$$\begin{aligned}
&\langle \Phi_{\mu} | \tau_{q}^{\dagger}(\mu) e^{S_{\mu}} e^{-T_{\mu}} \hat{H} e^{T_{\mu}} | \Phi_{\mu} \rangle + && \forall\, \tau_{q}^{\dagger}(\mu) \\
&\sum_{\lambda \neq \mu} \frac{C_{\lambda I}}{C_{\mu I}} \langle \Phi_{\mu} | \tau_{q}^{\dagger}(\mu) e^{S_{\mu}} e^{-T_{\mu}} e^{T_{\lambda}} | \Phi_{\mu} \rangle \langle \Phi_{\mu} | e^{-T_{\lambda}} \hat{H} e^{T_{\lambda}} | \Phi_{\lambda} \rangle \quad = 0
\end{aligned} \tag{6.23}$$

$$\begin{aligned}
&\langle \Phi_{\mu} | e^{S_{\mu}} [e^{-T_{\mu}} \hat{H} e^{T_{\mu}}, \tau_{q}(\mu)] | \Phi_{\mu} \rangle \\
&+ \sum_{\lambda \neq \mu} \frac{\tilde{C}_{I\lambda}}{\tilde{C}_{I\mu}} \langle \Phi_{\lambda} | e^{S_{\lambda}} e^{-T_{\lambda}} e^{T_{\mu}} | \Phi_{\lambda} \rangle \langle \Phi_{\lambda} | [e^{-T_{\mu}} \hat{H} e^{T_{\mu}}, \tau_{q}(\mu)] | \Phi_{\mu} \rangle \\
&+ \sum_{\lambda \neq \mu} \frac{\tilde{C}_{I\lambda}}{\tilde{C}_{I\mu}} \langle \Phi_{\lambda} | e^{S_{\lambda}} e^{-T_{\lambda}} e^{T_{\mu}} \tau_{q}(\mu) | \Phi_{\lambda} \rangle \langle \Phi_{\lambda} | e^{-T_{\mu}} \hat{H} e^{T_{\mu}} | \Phi_{\mu} \rangle \qquad \forall\, \tau_{q}(\mu) \\
&- \sum_{\lambda \neq \mu} \frac{C_{\lambda I}}{C_{\mu I}} \langle \Phi_{\mu} | e^{S_{\mu}} \tau_{q}(\mu) e^{-T_{\mu}} e^{T_{\lambda}} | \Phi_{\mu} \rangle \langle \Phi_{\mu} | e^{-T_{\lambda}} \hat{H} e^{T_{\lambda}} | \Phi_{\lambda} \rangle \quad = 0
\end{aligned} \tag{6.24}$$

In Eq (6.23), T_{μ} is clearly coupled to all other cluster operators $T_{\lambda}, \forall \lambda \neq \mu$ through the second term. In addition, it is coupled to de-excitation operator S_{μ} of the same vacuum. The new feature is that T_{μ} is directly coupled (though its defining equation) to right side model space coefficients. Its coupling to other parameters enters indirectly through Eq (6.24) defining de-excitation operator S_{μ}. On the other hand, S_{μ} is directly coupled to all other cluster operators, de-excitation operators, and left and right side model space coefficients through last three terms.

Therefore, in this variant of stationary state-selective MRCC theory, coupling between different parameters is somewhat balanced for in the sense that, information about the state directly enters into defining equations. This of course happens because it happens in the corresponding non-stationary theory as well. This may probably improve convergence of the theory over the previous one which leans more towards effective Hamiltonian description.

VI.4.3 Double linking and prospects for size-extensivity

Having been derived from exact theories, both stationary state-selective MRCC theories considered above are potentially exact. However, when cluster and de-excitation operators are truncated to low ranks for practical calculations, they are not size-extensive. This is despite the fact that the theories on which they have been based are rigorously size-extensive. The reasons for this are the same as in stationary single reference theories. The equations obtained by applying stationarity condition contain disconnected terms, which upon iteration, lead to size-inextensive results. In context of single reference theories, size-extensivity problems were obviated by using double-linked ECC functional. Similar possibilities may be expected in multi-reference situations.

In case of single-reference ECC, double-linking was achieved by a change of variables.[6,8] This absorbed the terms causing size-inextensivity into the definition of a new independent cluster-operator. Since there is one-one correspondence between old and new variables, the new functional is identical to the old one. This permitted variation procedure to be set up in terms of new variables leading to size-extensive results. Using MBPT, Arponen[6] analyzed the perturbative content of new cluster amplitudes and resulting energies at the stationary point. He proved that the energy contains all distinct MBPT diagrams when cluster amplitudes are not truncated. He further showed that, at any level of truncation, energy contains a proper and distinct subset of MBPT diagrams. This means that, just as standard SRCC, SR-ECC may be viewed a partial infinite order resummation of certain sets of MBPT diagrams.[6,8] This step is important, because terms in the double-linked ECC functional are just a subset of terms in original functional. This proof shows that, a potentially exact theory may be obtained despite deletion of certain terms (terms which cause size-inextensive behaviour) from energy functional.

A reflection reveals that it is difficult to obtain size-extensive versions of above stationary state-selective MRCC theories without achieving some kind of double-linking for the matrix elements of intermediate Hamiltonian containing both the cluster and de-excitation operators. However, it does not appear to be straightforward to achieve this goal. One simple way will be to drop terms causing size-inextensive behaviour. Such a procedure can be seen to automatically lead to a double-linked intermediate Hamiltonian, and to size-extensivity. However, this strategy immediately runs into problems. For, there is no guarantee that such a deletion will lead to a theory which is potentially exact. In other words, one has to now prove that exact full-CI results are recovered by inclusion of all untruncated cluster and de-excitation amplitudes. In absence of a well-defined state-selective multi-reference perturbation theory, this proposition looks virtually impossible.

Other logical possibility is to look for transformation to change variables, as was done in SR-ECC, to write to the intermediate Hamiltonian in a double-linked form. Consider diagonal terms of intermediate Hamiltonian in Eq (6.16) (non-diagonal terms do not contain de-excitation amplitudes in this case, and need not be considered). The first term is analogous to ECC energy functional, and it can be easily converted into double-linked form. De-excitation amplitudes S_μ which are fully contracted to a single cluster amplitude T_μ can be absorbed to redefine a new cluster operator $\tilde{T}_\mu$. It is easy to show that this new cluster operator now contains additional cluster amplitudes with valence-only labels. This happens because, S_μ and T_μ, despite containing no excitation operators with valence-only labels, upon multiplication yield operators which exclusive valence labels.

Keeping this difficulty aside, we proceed to the second term. It is easy to show that, for each term under the summation, the same operator $\tilde{T}_\mu$ can be recovered in the absorption process. Similarly, S_μ operators entirely connected to a single T_λ can be absorbed to define a new operator $\tilde{T}_{\mu\lambda}$ (note that this operator is different from operator $\tilde{T}_\lambda$ which is obtained by absorbing S_λ into T_λ). Continuing this process, we arrive at a double-linked expression for each diagonal element, and hence the entire intermediate Hamiltonian. Each cluster operator defined contains valence-only labeled cluster amplitudes as well. However, a look at the resulting intermediate Hamiltonian shows that it not only contains original cluster operators, but also many more cluster operators. This is an awkward situation. It is clear that all of them are not independent and can not be used for variation of the functional.

One may equate different cluster amplitudes for a given vacuum (retain the valence-only cluster amplitudes in them), and use the resulting double-linked intermediate Hamiltonian for variation purpose. However, this is only an assumption; the assumption that original intermediate Hamiltonian can be expressed in a different equivalent form by a change of variables.

It appears that different forms of intermediate Hamiltonian (even double-linked ones) may be constructed or proposed by suitable parameterization of its elements. However, unless they are shown to lead to Schrödinger equation upon variation, they are unlikely to be useful. The problem is related to the nature of wavefunction and variation principle. Suppose that an arbitrary energy functional with number of parameters same as cluster and de-excitation amplitudes, is proposed. It may be asked as to what are the conditions under which variation of this functional is equivalent to Schrödinger equation. It is clear that some kind of normalization condition should be implicit in the definition of the functional, without which stationary values (energies) are not meaningful. If parameters of the proposed functional do not have a clear interpretation as parameters of a related wave function, normalization can not be tested and there is no direct way to prove that the functional leads to Schrödinger equation. In ECC, this problem is avoided by deriving the functional from a bivariational energy functional. Furthermore, proof of potential exactness is also given.

In multi-reference situation, in absence of any such method to prove the potential exactness of a theory, it is clear that arbitrary forms for intermediate Hamiltonian obtained via some kind of parameterization may not work. An understanding of how to impose normalization condition on cluster and de-excitation amplitudes may be necessary to obtain completely size-extensive stationary state-selective multi-reference theories.

VI.5 Conclusions

State-dependent nature of the constrained variation functional for MRCC theories reveals that stationary MRCC theories are state-specific. Two such stationary state-selective MRCC theories have been obtained. Our approach has been to derive these theories via bivariational energy functional corresponding to the eigenvalue problem of an intermediate Hamiltonian. However, fully size-extensive state-selective MRCC theory which generalizes ECC is still not discernable. Main difficulties are related to construction of a suitable double-linked intermediate Hamiltonian. The results of this chapter constitute an initial attempt towards a formulation of stationary state-specific MR-ECC.

References

1. T. Helgaker and P. Jorgensen, Adv. Quant. Chem. **19**, 183 (1988)

2. (a) T. Helgaker and P. Jorgensen, Adv. Quant. Chem. **19**, 183 (1988) (b) P. Jorgensen and T. Helgaker J. Chem. Phys. **89**, 1560 (1988) (c) H. Koch, H. J. A. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria, H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990) (d) H. Koch and P. Jorgensen, J. Chem. Phys. **93**, 3333 (1990)
3. N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984)
4. R. J. Bartlett, in *Geometrical Derivatives of Energy Surface and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht,1986), p35
5. (a) L. Adamowicz, W. D. Laidig, and R. J. Bartlett, Int. J. Quant. Chem. **S18**, 245 (1984) (b) G. Fitzgerald, R. J. Harrison, and R. J. Bartlett, J. Chem. Phys. **85**, 5143 (1986) (c) E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989) (d) E. A. Salter and R. J. Bartlett, J. Chem. Phys. **90**, 1767 (1989)
6. J. Arponen, Ann. Phys. (N.Y.) **151**, 311 (1983)
7. (a) J. Arponen, R. F. Bishop, and E. Pajanne, Phys. Rev. **A36**, 2519 (1987) (b) ibid, **A36**, 2539 (1987)
8. R. F. Bishop, J. Arponen, and E. Pajanne, in *Aspects of many-body effects in molecules and extended systems, Lecture notes in Chemistry,* edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p78
9. U. S. Mahapatra, B. Datta, B. Bandopadhyay, and D. Mukherjee, Adv. Quant. Chem. **30**, p163 (1998)
10. U. S. Mahapatra, B. Datta, and D. Mukherjee, Mol. Phys. 94, 157 (1998)
11. U. S. Mahapatra, B. Datta, and D. Mukherjee, J. Chem. Phys. 110, 6171 (1999)
12. R. Weinstock, *Calculus of variations*, (Dover, 1974)
13. S. T. Epstein, *The Variation Principle in Quantum Chemistry*, (Academic, New York, 1974)

14. J. Cizek, Adv. Chem. Phys. **14**, 35 (1969)
15. (a) Kutzelnigg, in Methods of electronic structure theory, edited by H. F. Schaefer III (Plenum, New York, 1977) p129 (b) S. Koch and W. Kutzelnigg, Theor. Chim. Acta. **59**, 397 (1981) (c) W. Kutzelnigg, Theor. Chim. Acta. **80**, 349 (1991)
16. (a) R. J. Bartlett, S. A. Kucharski, J. Noga, J. D. Watts, and G. W. Trucks in *Aspects of many-body effects in molecules and extended systems, Lecture notes in Chemistry,* edited by D. Mukherjee (Springer-Verlag, 1989) Vol.**50**, p125 (b) P. G. Szalay, M. Nooijen, and R. J. Bartlett, J. Chem. Phys. **103**, 281 (1995)
17. S. Pal, M. D. Prasad, and D. Mukherjee, Pramana, **18**, 261 (1982)
18. (a) S. Pal, M. D. Prasad, and D. Mukherjee, Theor. Chim. Acta. **62**, 523 (1983) (b) ibid. **66**, 311 (1984)
19. S. Pal, Theor. Chim. Acta. **66**, 151 (1984)
20. (a) S. Pal, and K. B. Ghose, Cur. Sci. **63**, 667 (1992) (a) K. B. Ghose, P. G. Nair, and S. Pal, Chem. Phys. Lett. **211**, 15 (1993) (b) N. Vaval, K. B. Ghose, P. G. Nair, and S. Pal, Proc. Ind. Acad. Sci. **106**, 387 (1994)
21. (a) R. J. Bartlett, and J. Noga, Chem. Phys. Lett. **150**, 29 (1988) (b) R. J. Bartlett, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **155**, 133 (1989)
22. S. Pal, and N. Vaval, Recent Res. Dev. Phys. Chem. **6**, 527 (2002)
23. (a) L. Z. Stolarczyk and H. J. Monkhorst, Phys. Rev. **A32**, 725 (1986) (b) G. S. Latha and M. D. Prasad in *Strongly correlated electron systems in chemistry : Experiment and Theory*, edited by S. Ramasesha and D. D. Sharma (Narosa, India, 1996) p32
24. (a) S. Pal, Theor. Chim. Acta **62**, 523 (1983) (b) ibid, Phys. Rev. **A33**, 2240 (1986) (b) ibid, **A34**, 2682 (1986) (c) K. B. Ghose, and S. Pal, Phys. Rev. **A36**, 1539 (1987)

(d) S. Pal, Phys. Rev. **A39**, 2712 (1989) (e) ibid, Phys. Rev. **A42**, 4385 (1990) (d) S. Pal, and K. B. Ghose, Phys. Rev. **A45**, 1518 (1992)

25. (a) N. Vaval, K. B. Ghose, and S. Pal, J. Chem. Phys. **101**, 4914 (1994) (b) N. Vaval, and S. Pal, Phys. Rev. **A54**, 250 (1996) (c) A. B. Kumar, N. Vaval, and S. Pal, Chem. Phys. Lett. **295**, 189 (1998) (d) N. Vaval, A. B. Kumar, and S. Pal, Int. J. Mol. Sci. **2**, 89 (2001) (e) N. Vaval, Chem. Phys. Lett. **318**, 168 (2000) (f) P. U. Manohar, N. Vaval, and S. Pal, Chem. Phys. Lett. **387**, 442 (2004)
26. P. Piecuch, and R. J. Bartlett, Adv. Quant. Chem. 34, 295 (1999)
27. (a) A. I. Krylov, C. D. Sherrill, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 10669 (1998) (b) V. T. Voorhis, and M. Head-Gordon, Chem. Phys. Lett. **317**, 575 (2000) (c) ibid, Chem. Phys. Lett. **330**, 585 (2000) (d) ibid, J. Chem. Phys. **113**, 8873 (2000) (e) ibid, J. Chem. Phys. **115**, 5033 (2001)
28. D. Mukherjee and S. Pal, Adv. Quant. Chem. **20**, 291 (1989)
29. H. J. Silverstone and O. Sinanoglu, J. Chem. Phys. **44**, 3608 (1966)
30. F. E. Harris, Int. J. Quant. Chem. **S11**, 403 (1977)
31. (a) J. Paldus, J. Cizek, M. Saute, and A. Laforgue, Phys. Rev. **A17**, 805 (1978) (b) M. Saute, J. Paldus, J. Cizek, Int. J. Quant. Chem. **15**, 463 (1979)
32. (a) H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053, 4279 (1978) (b) ibid. **68**, 4279 (1978)
33. (a) A. Banerjee and J. Simons, Int. J. Quant. Chem. **19**, 207 (1981) (b) ibid, J. Chem. Phys. **76**, 4548 (1982)
34. H. Baker and M. A. Robb, Mol. Phys. **50**, 20 (1983)
35. (a) W. D. Laidig and R. J. Bartlett, Chem. Phys. Lett. **104**, 424 (1984) (b) W. D. Laidig, P. Saxe, and R. J. Bartlett, J. Chem. Phys. **86**, 887 (1987)

36. R. Tanaka and H. Terashima, Chem. Phys. Lett. **106**, 558 (1984)
37. M. R. Hoffmann and J. Simons, J. Chem. Phys. **88**, 993 (1988)
38. (a) N. Oliphant and L. Adamowicz, J. Chem. Phys. **94**, 1229 (1991) (b) ibid, **96**, 3739 (1992)
39. P. G. Szalay in *Recent advances in coupled-cluster methods*, edited by R. J. Bartlett, (World Scientific, Singapore, 1997), p81
40. (a) J. Meller, J. P. Malrieu, and R. Caballol, J. Chem. Phys. **104**, 4068 (1996) (b) L. Adamowicz and J. P. Malrieu, in *Recent advances in coupled-cluster methods*, edited by R. J. Bartlett, (World Scientific, Singapore, 1997), p307
41. U. S. Mahapatra, B. Datta, and D. Mukherjee, in *Recent advances in coupled-cluster methods*, edited by R. J. Bartlett, (World Scientific, Singapore, 1997), p155
42. (a) J. Masik and I. Hubac, in Quantum theory in chemistry and physics, edited by R. McWeeny (San Miniato, Italy, 1996) (b) J. Masik and I. Hubac, Adv. Quant. Chem. **31**, 75 (1999)
43. M. Nooijen, Int. J. Mol. Sci. **3**, 656 (2002)
44. D. Mukherjee, Chem. Phys. Lett. **274**, 561 (1997)
45. W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **107**, 432 (1997)
46. P. G. Szalay, Int. J. Quant. Chem. **55**, 151 (1995)