Abstract

This thesis is mainly focused on the calculation of molecular response properties using Intermediate Hamiltonian formulation of Fock space multi-reference coupled cluster (IHFSMRCC) theory. These properties include excitation energies, excited state properties and the electronic transition dipole moment. Apart from the IHFSMRCC, a variant of variational coupled-cluster i.e. extended coupled-cluster (ECC) method has also been used for the ground state molecular response properties for closed shell systems at equilibrium as well as stretched geometries.

Over the past few decades, coupled cluster methods [1-4] have been established as promising tools for evaluation of correlation energy as well as molecular properties. It introduces the dynamic correlation in efficient way through infinite partial summation of important terms of many body perturbation theories. The linear response approach to the coupled cluster method was originally formulated by Monkhorst [5] and further developed and applied with orbital relaxation built in by Bartlett and coworkers, who introduced the Z-vector [6] technique within the coupled cluster (CC) framework [7] to simplify the energy derivative problem. With the help of Z vector method, energy derivative for each mode of perturbation can be obtained by solving only an additional linear equation, which contains one extra set of perturbation-independent parameters. This algebraic method is however quite laborious and more difficult for higher order derivatives. Jorgensen and coworkers [8] formulated constrained variational approach based on method of Lagrange multipliers. The final equation is shown to be equivalent as the ones obtained through Z vector technique, but this approach is found to be suitable for extension to progressive higher order derivatives.

Parallel to these developments, Pal et al [9-11] also pursued a fully stationary approach to expectation value coupled cluster (XCC). It has been realized that variational methods are quite desirable especially for molecular properties
because of its fulfillment of GHF theorem and \( (2n+1) \) rule. Pal and coworkers implemented the variational method which is based on direct variation of suitable energy functional without any constraint [9]. Various forms of energy functional like expectation value (XCC) [9-12], Unitary coupled cluster (UCC) [13, 14] and extended coupled cluster (ECC) [15, 16] have been studied in literature. Among these, ECC has shown to be most promising as well as successful functional in particular for properties.

The idea of ECC functional was first developed by Arponen [15] and then used by Arponen and coworkers [16] in the context of condensed matter physics. Among its many advantageous features, double linked structure of ECC functional is a particular one, which not only ensures a naturally terminating series of energy functional, but also provides a fully connected set of stationary equations for cluster amplitudes even in its approximate versions.

Although ECC functional has naturally terminating series due to its double linking structure, natural truncation occurs at very high powers in excitation and de-excitation amplitudes. Hence ECC functional with singles and doubles requires further approximations to be imposed in order to make it computationally feasible for its larger application. Various forms of approximation schemes has already been implemented and analyzed by several workers [17-19].

A perturbation based analysis generally provides a guideline to identify the importance of individual terms in energy functional. The different variations of UCC and XCC functional known as XCC(\(n\))/UCC(\(n\)) have been used for energy calculations by Bartlett and coworkers [12, 13]. These functional contain all the terms correct through a given order \(n\). Similar kind of perturbation based functional for ECC (\(n\)) has also been used and analyzed by Kucharaski and Bartlett [20] for correlation energy at the equilibrium as well as stretched geometry.
However, in cases of molecular bond dissociation and open shell states, a multi-reference zeroth order description becomes essential for the treatment of non-dynamic electron correlation and dynamic correlation is taken care of by the built-in exponential feature of wave operator. These methods are collectively referred to as multi-reference coupled cluster (MRCC) [21-29] methods. Existing MRCC approaches can be divided into three basic categories: Fock space (FS) [21, 22] or valance universal (VU), Hilbert space (HS) [23] or state universal (SU) and state selective (SS) [24-29] CC. The first two approaches are commonly in the class of multi-root MRCC methods, as they are built on the concept of Bloch equation based effective Hamiltonian [30-31] acting within a model space. It is important to mention here that several methods based on SRCC have been extensively developed, which are widely applicable in quasi-degenerate situations [32-39]. Although these methods structurally differ from MRCC method in many aspects, their high accuracy, relative simplicity and cost effectiveness are important to note.

In this thesis, we focus mainly to the FSMRCC method. [40-53] The FSMRCC method has been successfully used for difference energy calculations. However, in several cases when model space is increased in order to target more excited states, the method faces convergence difficulties. This is termed as intruder state [54, 55] problem. The intermediate Hamiltonian [56] formulation of FSMRCC (IHFSMRCC) [57-60] method provides a more efficient and reliable as well as numerically stable way to handle the intruder state problem.

The idea of intermediate Hamiltonian was first introduced by Malrieu [56] et al in the context of degenerate perturbation theory. Various kinds of intermediate Hamiltonian schemes have been developed and implemented by several workers [57-60].

Formulation of efficient theoretical as well computational technique for the evaluation of molecular properties in FSMRCC method is quite desirable in order to increase the scope and applicability of the method. The linear response
in effective Hamiltonian based FSMRCC method was initiated by Pal [61] and then implemented by Pal and coworkers for the first order properties [62, 63]. Ajitha and Pal developed the Z-vector like formalism in FSMRCC [64, 65] framework, which eliminated the highest sector cluster response quantities. The extension of Lagrange multiplier approach (LMA) in FSMRCC theory using complete model space for the first order energy derivatives was initiated by Szalay [66]. This approach was further generalized for general incomplete model space by Shamasundar et al [67, 68] for higher order energy derivatives and also implemented by Pal and coworkers [69-72].

In our opinion, it is desirable to extend the LMA in IHFSMRCC formulation for energy derivatives, in order to obtain excited state properties for desired number of states with bigger basis sets and larger model space in numerically stable and cost effective way. The same is one of the major objectives of this thesis. Apart from the IHFSMRCC method, a variational single reference CC method for efficient evaluation of ground state molecular electric response properties has also been proposed and implemented. The present thesis is organized as follows:

**First chapter:** In this chapter, we have briefly reviewed the early developments in molecular quantum chemistry especially for electronic structure theory. A general introduction has been provided for both single and multireference methods. The linear response approach has been discussed for single reference and Fock space multi-reference coupled cluster theory. Z-vector and Lagrange multiplier approach for energy derivatives has also been discussed for coupled cluster (CC) methods. Finally, at the end of this chapter, the scope and objectives of this thesis have been discussed.

**Second Chapter:** In this chapter, we have presented and analyzed the extended coupled cluster (ECC) energy functional, truncated up to nth perturbation order limit to operators of the single and double excitations. The expression for the first order energy derivatives based on the above truncation schemes has been derived and numerically analyzed. We have done a comparative study for
dipole moment in various perturbative ECC (n) methods \((2 \leq n \leq 5)\) for three systems (HF, H\(_2\)O and BH) at equilibrium geometry. We have particularly studied two variants of ECC (4) and ECC (5*) method for stretched geometry. We have analyzed the contribution of important terms present in ECC functional based on perturbative argument. We have compared our results with standard coupled cluster (CCSD) as well as cubic truncated ECC and also benchmarked with the full CI results wherever available.

**Third chapter:** in this chapter, we present a formulation based on Lagrange multiplier approach for efficient evaluation of excited state energy derivatives in Fock space coupled cluster theory within the Intermediate Hamiltonian framework. The formulation is applied to derive the explicit generic expressions up to second order energy derivatives for \([1, 1]\) sector of Fock space with singles and doubles approximation. Its advantage, efficiency and interconnection in comparison to the Lagrange multiplier approach in traditional formulation of Fock space, which is built on the concept of Bloch equation based effective Hamiltonian, has been discussed. Computational strategy for their implementation has also been discussed in some detail.

**Fourth chapter:** In this chapter, we have calculated electronic transition dipole moment (ETDM) through intermediate Hamiltonian formulation of Fock space multi-reference coupled-cluster (IHFSMRCC) theory, which measures absorption intensities. ETDM can be directly obtained through matrix element of one particle electric perturbation operator between ground and excited states. A Lagrange multiplier approach has been used to parameterize the left vector of both the ground and excited states, while the right vector of excited state is obtained through eigenvalue structure of intermediate Hamiltonian matrix. Apart from ETDM, excitation energies have also been calculated through IHFSMRCC in order to relate the ETDM to oscillator strength using dipole length approximation. We have presented the transition dipole moments and oscillator strengths of few molecules and compare our results with values obtained through equation of motion coupled-cluster (EOMCC) method.
Fifth chapter: The Fock space multi-reference coupled cluster (FSMRCC) method provides an efficient approach for direct calculation of excitation energies. In the intermediate Hamiltonian (IH-FSMRCC) formulation, the method is free from intruder state problem and associated convergence difficulties, even for a large active space. In this chapter, we demonstrate that the IH-FSMRCC method with suitably chosen model space can be used for accurate description of core excitation spectra of molecules even with Hartree-Fock orbital for the neutral molecules. We have reported the core excitation energy of three test systems H$_2$O, N$_2$ and CH$_4$. Unlike the EOM based method, the IH-FSMRCC does not require any special technique for convergence. Our preliminary test results shows that the IHFSMRCC method with singles and doubles approximation performs slightly better than the standard EOMEE-CCSD method.
References:


