STUDY OF MOLECULAR VIBRATION USING COUPLED CLUSTER THEORY

Thesis submitted to the

University of Pune

for the Degree of

Doctor of Philosophy

in

Chemsitry

By

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December 2010

CERTIFICATE

CERTIFIED THAT the work done in the thesis entitled,

Study of molecular vibration using coupled cluster theory

submitted by **Subrata Banik** was carried out by the candidate under my supervision in the Physical Chemsitry Division, National Chemical Laboratory, Pune 411008, India. Any material that has been obtained from other sources has been duly acknowledged in the thesis.

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DECLARATION

I hereby declare that the work incorporated in the thesis entiled

Study of molecular vibration using coupled cluster theory

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

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Subrata Banik

Acknowledgements

It is the right place to express my heartfelt gratitude and thanks to my supervisor Dr. Sourav Pal. He has been a wonderful teacher who opened to me the gate of wonderland of quantum chemistry. He always gave academic freedom to think independently and encouraged to express my view to improve the communication skill. In his words 'communication is the most important thing in any scientific research'. Over the course of my PhD research, he guided me by his wisdom, not only to solve a particular problem but also to go to the next forward. I was motivated by his quotation 'Goddess Swarasati never betrays'.

No words can express my gratitude to Prof M. Durga Prasad. Each of my visit to School of Chemistry, University of Hyderabad is very precious to me. I thank him for much of what I know about molecular vibrations and vibrational coupled cluster method. His highly motivating teaching made me enjoy each and every step of the work I was doing under his guidance. Apart from that, I learnt from him *'what matters and what does not matter'*.

I am grateful to Dr. Nayana Vaval for her help, support and encouragement. At every moment she made me feel at home. I can not forget her help at all kind of critical situations.

I thank the Director of NCL, Dr. S. Sivaram, for extending various facilities in the laboratory. The financial support from University Grant Commission, India as JRF and SRF fellowship and J. C. Bose Grant of Dr. Sourav Pal for a sustaining fellowship are highly acknowledged. I also acknowledge CSIR travel grant and NCL foreign travel grant to attend 8th ICCMSE conference held at Psalidi, Greece.

My thanks goes to Mr. Deepak Jori, Secretary, Head of Physical Chemistry, for his kind help over many official issues and also to Mr. Punekar and Mr. Golab for their time to time help.

I thank all of my lab-mates for the most enjoyable time I spend here. Thanks to my

Contents

List of Tables

List of Publications

1. Calculation of vibrational energy of molecule using coupled cluster linear response theory in bosonic representation: convergence studies

   - **S. Banik**, S. Pal, M. Durga Prasad

   J. Chem. Phys. **129**, 134111 (2008)

2. Calculation of dipole transition matrix elements and expectation values by vibrational coupled cluster method

   - **S. Banik**, S. Pal, M. Durga Prasad

   J. Chem. Theor. Comput. **6**, 3198 (2010).

Abstract

Title: Study of Molecular Vibration Using Coupled Cluster Theory.

The main objective of this thesis is to develop accurate method for the description of molecular vibration using coupled cluster theory. Accurate description of molecular vibration is often necessary to account the experimental results obtained in the modern highly accurate techniques in molecular spectroscopy.

The coupled cluster method has been established as one of the most accurate technique for the description of quantum many body systems[1–3]. In particular this method has immense success over last few decades in the field of electronic structure of atoms and molecules[4]. In this approach the ground state wave function of a many body system is decomposed into a reference function and an exponential wave operator. There are two advantages in the coupled cluster approach. First, by virtue of its exponential ansatz, the method satisfies one of the most demanding criteria of proper separation of fragments in zero interaction limit namely 'the size consistency'. Second, again due to the exponential structure of wave operator, the resulting wave function and energy are highly accurate in an approximate calculation.

Recently several attempts have been made to describe molecular anharmonic vibrations by coupled cluster method[5–11]. There are two representation possible for the vibrational coupled cluster formalism. These two approaches differ in the construction of the Fock space. The first method is the basis set representation[8–11], in which the Fock space is constructed as a union of all k-particle Hilbert spaces constructed as the tensor products of basis functions of the appropriate degrees of freedom. The second approach is to construct the Fock space using harmonic oscillator (HO) ladder operators acting on an appropriate vacuum state. This representation is termed as bosonic representation[5–7]. The presented work in this thesis focuses on the implementation of coupled cluster method in bosonic representation to calculate vibrational transition energies, expectation values, transition intensities.

There are mainly two approaches to study the excited states within coupled cluster

framework. The first one is the coupled cluster linear response theory[12–15], where the excited state wave function is obtained by the action of a linear operator on the ground state coupled cluster wave function. Here, a similarity transformed Hamiltonian is generated and diagonalized within excited states manifold to get excited states energies and eigenvectors. All vibrational calculations till date used this approach. In this thesis, we study the convergence pattern of state energies with respect to the rank of the cluster operator at ground state level as well as the excitation operator at CCLRT level. However, the main drawback of the CCLRT approach is that, here, the similarity transformed Hamiltonian is manifestly non-Hermitian. Because of non-hermicity, it generates complex eigenvalues in diagonalization. One approximate way to overcome the problem of complex eigenvalues is to use a second similarity transformation with de-excitation operator in the spirit of extended coupled cluster approach (ECCM) formulated by Arponen[16]. The second similarity transformation reduces the loss of hermicity of the Hamiltonian up to second order. In this thesis, we highlight the significance of ECCM approach over normal coupled cluster (NCCM) approach.

The second approach of calculating the excited state is the multi-reference coupled cluster method[17, 18] (MRCCM) based on effective Hamiltonian theory that acts in a model space. The valance universal version of MRCCM has been used very successfully for excitation energies and response properties of electronic structure problems. Another goal of the thesis is to develop the multi-reference coupled cluster method for the description of anharmonic molecular vibrations.

Parallel to energy calculations spectacular developments have been made to calculate non-energetic properties within coupled cluster framework. The drawback of using CCM wave function to calculate expectation values is that, it leads to a non-terminating series[19] making it impractical for the numerical work. Calculation of transition matrix elements between two states also suffer from same problem. Prasad[20] proposed an alternate approach within CCM framework to calculate expectation values and transition matrix elements that bypasses the need to evaluate such infinite series. This approach is

termed as effective operator approach. Here, an effective operator is formed in the same fashion of effective Hamiltonian formed in CCLRT. The expectation values of operators are calculated using this effective operator with the eigenvectors obtained in CCLRT. The other goal of the thesis is to use the effective operator formalism to calculate the expectation values and transition intensities.

The thesis is organized as follows:

In the first chapter, we briefly describe the earlier developments of *ab initio* methods for the description of anharmonic molecular vibrations. We review different kind of coordinate systems usually used to express the vibrational Hamiltonian and the justification of choosing normal coordinate over others in our work. Variational principle based methods e.g. vibrational self consistent field (VSCF) method and its generalization to multi-reference functions, vibrational configuration interaction (VCI) are reviewed briefly here. We discuss certain aspects of perturbative approaches for vibrational analysis. A detail discussion is given on the two kind of representations of vibrational coupled cluster formalism. Finally, the scope of the thesis is discussed at the end of the chapter.

In the second chapter, we discuss the vibrational coupled cluster formulation in bosonic representation. We discuss extended coupled cluster methodology and its significance over normal coupled cluster method (NCCM). The methodologies are applied to some tri-atomic molecules e.g. H_2O, F_2O, O_3 etc. and tetra-atomic molecule H_2CO to calculate vibrational state energies. The convergence studies of vibrational state energies with respect to the rank of cluster operator of the ground state as well as excitation operator at CCLRT level of these molecules are presented here. We discuss the significance of ECCM approach over NCCM approach in terms of convergence pattern of state energetics with respect to the rank of both cluster operator as well as excitation operator. The chapter highlights the computational efficiency of CCM over converged full CI in terms of CPU time.

The third chapter of the thesis is devoted to the formulation of effective operator approach based on coupled cluster method to calculate expectation values of operators and

transition matrix elements. The proposed methodology is applied to water molecule and its isotopic variants to calculate dipole moment expectation values and transition matrix elements. Detail studies are presented on the convergence pattern of these quantities with respect to excitation operator at CCLRT level. The ECCM based approach is also implemented to calculate these quantities. Discussion is made on the significance of ECCM over NCCM in calculating in quantities.

In the fourth chapter, we discuss the development of multi-reference coupled cluster theory for anharmonic molecular vibrations. We use the Fock space version of multi-reference coupled cluster method in the same spirit of electronic structure theory. The model space used here is inherently complete. A detail discussion is made on the solution of FSMRCC equation in bosonic representation.

In the last chapter, we discuss about some future aspect of the vibrational coupled cluster method in bosonic representation. In particular, we highlight the possibilities of inclusion of rotational contributions to vibrational Hamiltonian. We further point that the expectation values of operator and transition matrix elements can be calculated within FSMRCCM approach in a highly accurate manner.

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Chapter 1

General introduction and the scope of the thesis

1.1 Introduction

Vibrational spectra of polyatomic molecules[1–6] contain enormous amount of information about molecular structures and chemical compositions. Over last few decades, there have been spectacular developments on high resolution molecular spectroscopy which has provided more and more accurate and precise information about gas phase molecules. This has been a driving force for the advancement of chemical physics to develop advanced methods to describe the vibrational structure in more and more accurate manner. Like other branches of chemistry, the quantum mechanical techniques [7–9] have been applied over the years for the proper description of molecular vibrations. The Born-Oppenheimer approximation [10–14] provides the platform to apply quantum mechanics to the molecular systems. Within this approximation, the electronic energy provides the potential for the motion of nuclei. Once this potential energy function is known, the rovibrational energy levels of the molecules can be calculated by solving

Schrödinger equation for nuclear motion. However, writing the ro-vibrational Hamiltonian is not straight forward. It depends on the coordinate system used to describe the nuclear motion. The correct quantum mechanical Hamiltonian was obtained for generalized coordinate system by Podolsky[15]. Eckart [16] has developed a coordinate system based on molecule-fixed rotating axis to study the vibrations around equilibrium. For semi-rigid molecules around equilibrium the vibrational coordinates can be written as linear combination of nuclear Cartesian coordinates. One defines the normal coordinate system as linear transformation of nuclear Cartesian coordinates in which the Hessian matrix i.e. the second derivative matrix of electronic energy with respect to the these coordinates is diagonal. Watson [20] has derived the most simple form of vibrational Hamiltonian in the normal mode basis in the Eckart frame [3, 16–18].

Several quantum mechanical methods have been developed to study the molecular vibrations using the Watson Hamiltonian. There are mainly two approach to deal with solution of many-body Schroödinger equation. One is the variational approach [24] and the other one is the perturbative approach [21–23]. Within variational approach, methods like vibrational self consistence field (VSCF) [25–32] method, vibrational multireference self consistence field method (VMCSCF) [34–36], vibrational configuration interaction method (VCI) [32, 38–42] have been evolved and applied extensively over years. Within perturbative approach both Van Vleck [47–52] and Møller-Plesset perturbation method [53–59] have been applied to study the molecular vibrations. Each of these methods has its advantages and drawbacks.

The third approach, known as coupled cluster method [60–64], is neither variational nor perturbative. This method has been established as the state-of-the-art method for the description of many body system in general and electronic structure theory in particular. It has immense success in calculating electronic state energies, potential energy surfaces and other non-energetic properties.

There were some attempts to apply coupled cluster method to describe one dimensional anharmonic vibration [65–67]. The first implication to molecular anharmonic

vibrations was made by Prasad and co-workers [68]. There are two different representations possible for coupled cluster description [69] of anharmonic molecular vibrations. The first one is the bosonic representation [68–71]. Here, the Fock space is constructed using harmonic oscillator (HO) ladder operators acting on an appropriate vacuum state. Prasad and co-workers used this representation. The second approach is termed as basis set representation [75–82] in which the Fock space is constructed as a union of all k-mode Hilbert spaces constructed as the tensor products of basis functions of the appropriate degrees of freedom. This is the route followed mainly by Christiansen and co-workers.

The implementation of vibrational coupled cluster method in bosonic representation is still limited. In this thesis we aimed to make a systematic study of vibrational coupled cluster method in bosonic representation in terms of the convergence of cluster operator. We analyze the implications of coupled cluster linear response theory for the description of vibrational excited states and their convergence patterns in terms of the rank of the excitation operators.

To start with, we give a brief overview of different representation of molecular vibrational Hamiltonian and the *ab initio* methods to solve the vibrational Schrödinger equation. This helps in placing the relevance of the proposed work. Since the formulation of coupled cluster method is based on second quantization and diagrammatic techniques, we give a briefly review these techniques. In the subsequent subsections, we discuss basic coupled cluster methodology and the developments of various methods to calculate excited states, non-energetic properties within coupled cluster framework. A brief review of some earlier work on vibrational coupled cluster method is given after that. The objective and scope of the thesis are discussed at the end.

1.2 Full Molecular Hamiltonian

Let us consider a molecule consisting of N nuclei with masses m_α and charges $Z_\alpha e$, $\alpha = 1, 2, .., N$ and n electrons, each of having mass m_e and charge $-e$. The nuclei and electrons are described by $(X_\alpha, Y_\alpha, Z_\alpha)$ and (x_i, y_i, z_i) respectively in a Cartesian system of coordinates rigidly attached to the laboratory [Laboratory axis system (LAS)]. Let us denote R_n as the set of Cartesian coordinates of nuclei and r_e as the set of all Cartesian coordinates of electrons. Assuming that the molecule is not influenced by any external field, the non-relativistic Hamiltonian of the molecule can be written as [3, 5, 14, 18]

$$\hat{H} = \hat{T}_n + \hat{T}_e + V(R_n, r_e). \tag{1.1}$$

Here, $\hat{T}_n$ is the kinetic energy operator of nuclei and is given by

$$\hat{T}_n = \frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} [\frac{\partial^2}{\partial X_\alpha^2} + \frac{\partial^2}{\partial Y_\alpha^2} + \frac{\partial^2}{\partial Z_\alpha^2}], \tag{1.2}$$

$\hat{T}_e$ is the kinetic energy operator of electrons is given by

$$\hat{T}_e = \frac{\hbar^2}{2} \sum_{i=1}^{n} \frac{1}{M_i} [\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}], \tag{1.3}$$

and the $V(R_n, r_e)$ is the Coulomb potential energy function is given by

$$\begin{aligned}
V(R_n, r_e) = &-\sum_{\alpha=1}^{N}\sum_{i=1}^{n} \frac{Z_\alpha e^2}{\sqrt{(X_\alpha - x_i)^2 + (Y_\alpha - y_i)^2 + (Z_\alpha - z_i)^2}} \\
&+ \sum_{i<i'} \frac{e^2}{\sqrt{(x_i - x_{i'})^2 + (y_i - y_{i'})^2 + (z_i - z_{i'})^2}} \\
&+ \sum_{\alpha<\alpha'} \frac{Z_\alpha Z_{\alpha'} e^2}{\sqrt{(X_\alpha - X_{\alpha'})^2 + (Y_\alpha - Y_{\alpha'})^2 + (Z_\alpha - Z_{\alpha'})^2}}.
\end{aligned} \tag{1.4}$$

1.3 The Born-Oppenheimer Separation:

The Schrödinger equation associated with the Hamiltonian in Eq.1.1 is written as

$$\hat{H}\psi_{ne}(R_n, r_e) = E_{ne}\psi_{ne}(R_n, r_e). \tag{1.5}$$

4

The first simplification is the separation of nuclear and electronic motion due to Born-Oppenheimer (BO) approximation [10–13]. Born and Oppenheimer in 1927 [10] showed that if the rovibroinc Hamiltonian described in eq (1.1) is expanded in power of a parameter κ, defined as the fourth root of the ratio of mass of electron and mean mass of nucleus,

$$\kappa = (\frac{m_e}{\sum_\alpha m_\alpha/N})^{\frac{1}{4}} = (\frac{m_e}{M})^{\frac{1}{4}}, \tag{1.6}$$

the electronic energy appears in the zeroth order, vibrational energy appears in second order and rotational energy appears in the fourth order in the expression while the first order and third order terms disappear. The BO approximation leads to the well-known separated equations,

$$(\hat{T}_e + \hat{V}_e(R_n, r_e))\psi_e(R_n, r_e) = E_e(R_n)\psi_e(R_n, r_e) \tag{1.7}$$

$$(\hat{T}_N + \hat{E}_e + \hat{V}_N)\phi_N(R_n, r_e) = E_N\phi_N(R_n, r_e), \tag{1.8}$$

where, $\hat{V}_e(R_n, r_e))$ is the potential energy function for electronic motion which contain electron-electron repulsion and nuclear-electron attraction term. $\hat{V}_N$ is the nuclear-nuclear repulsion term. Eq. (1.18) is the Schrödinger equation for electronic motion where the electronic wave function is parametrically dependent on the nuclear coordinate. The defined electronic Hamiltonian is known as *clamped nucleus Hamiltonian* [11, 12], which means that all nuclei have a fixed geometry defined by the coordinates R_N. The electronic energy obtain under clamped nucleus approximation together with the nuclear-nuclear repulsion term $\hat{V}_N$ is the potential for the nuclear Schrödinger equation.

1.4 Translation free Hamiltonian

We obviously need $3N$ degrees of freedom to describe nuclear motion. Among these three degrees of freedom are needed to describe the translational motion of molecule. During translation of molecule, all nuclei move uniformly along a straight line without

changing their relative positions. One can eliminate translational degrees of freedom by simply choosing the Cartesian coordinates of the nuclear center of mass as three translational coordinates in the laboratory-fixed axis. The remaining $(3N - 3)$ coordinates, known as *translation free coordinates* [19] account for rotational and vibrational motions and are defined by $N - 1$ equations,

$$\begin{Bmatrix} t_i X \\ t_i Y \\ t_i Z \end{Bmatrix} = \sum_{\alpha=1}^{N} V_{\alpha i} \begin{Bmatrix} X_\alpha \\ Y_\alpha \\ Z_\alpha \end{Bmatrix}, i = 1, 2, \ldots, N - 1. \tag{1.9}$$

These coordinates are invariant under translational motion due to the condition,

$$\sum_{\alpha=i}^{N} V_{\alpha i} = 0. \tag{1.10}$$

Now, the kinetic energy operator in eq (1.8) can be factored into two parts, one translational kinetic energy operator and other is ro-vibrational kinetic energy operator,

$$\hat{T}_N = \hat{T}_{tr} + \hat{T}_{rv}. \tag{1.11}$$

Dropping out the translational part, the nuclear Schrödinger equation becomes,

$$(\hat{T}_{rv} + \hat{E}_e + \hat{V}_N)\phi_N(R_n, r_e) = E_N \phi_N(R_n, r_e). \tag{1.12}$$

1.5 Separation of rotational and vibrational motion

The $3N - 3$ translation free coordinates corresponds to two kind of molecular motion. One is the uniform rotation of molecule as whole and other is the relative displacement of the nuclei from each other, that is vibration. It is convenient to define a new Cartesian coordinate axis that is attached to molecule to separate the uniform rotation of molecule from the vibrational motion. This coordinate system is commonly known as *molecular axis system*[MAS] [5, 16, 20]. The origin in MAS is placed at the center of mass of the

molecule. The relative orientation of MAS with respect to LAS is defined by three Euler angle (θ, ϕ, χ)

$$
\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \lambda_{xX} & \lambda_{xY} & \lambda_{xZ} \\ \lambda_{yX} & \lambda_{yY} & \lambda_{yZ} \\ \lambda_{zX} & \lambda_{zY} & \lambda_{zZ} \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}. \tag{1.13}
$$

Here, the rotational matrix λ is called the direction cosine matrix. The rotational coordinates of a nonlinear polyatomic molecule are defined by these three Euler angles. However, for linear molecule having all nuclei lying along Z axis only two angle (θ, ϕ) are considered as rotational coordinates. A new set of $3N - 6$ coordinates ($3n - 5$ in case of linear molecule) are defined as vibrational coordinates. These coordinates are invariant under translation as well as uniform rotation of the molecule. So, the potential function only depends on the vibrational coordinates. However, due to vibrational angular momentum terms that arise because of bending motions, the vibrational kinetic energy term is dependent on the rotational coordinates (θ, ϕ, χ). As a consequence, complete decoupling of rotational and vibrational degrees of freedom in any case is impossible. Eckart [16] has prescribed two conditions to minimize this rotational and vibrational coupling for semi-rigid molecules in MAS around equilibrium. If we define m_i as the mass of i'th nucleus and z_i as its Cartesian coordinates, z_i^0 as the coordinates at equilibrium and ρ_i as the displacement coordinates (defined as $z_i - z_i^0$). Then the first Eckart condition [16, 17, 20] is due to separation of the motion of center of nuclear mass (translational motion),

$$
\sum_{i=1}^{N} m_i z_i = 0. \tag{1.14}
$$

The second Eckart condition [16, 17, 20] is for the cancellation of angular momentum at reference geometry, that is to separate the rotations and vibrations for small amplitudes of motion around equilibrium,

$$
\sum_{i=1}^{N} m_i z_i^0 \times \rho_i = 0. \tag{1.15}
$$

The Eckart's frame is the natural choice for normal coordinates to study vibrations of semi-rigid molecules around equilibrium.

1.6 The vibrational coordinates

The first problem that one encounters to solve the vibrational Schrödinger equations is to choose a proper coordinate system to define the vibrational Hamiltonian in Eq. 1.12 in terms of these coordinates. There are two fundamental classes [5] of vibrational coordinate systems emerge from the literature, namely the *rectilinear* and the *curvilinear coordinates*. The most conventional coordinate system is the rectilinear normal coordinate based of Eckart frame. It provides excellent description for vibrations of semi-rigid molecules at low level excitations around equilibrium geometry. However, for floppy molecules or highly excited vibrational states, one has to go for curvilinear coordinates. Depending on the context several kinds of curvilinear coordinates are defined in the literature. These are mainly *internal bond angle, bond length* [18, 41, 50, 97–102], *local mode* [50, 103–111] *Jacobi* coordinates [47, 50, 112–116, 127] etc. We will briefly review some of the vibrational coordinates usually used in the rovibrational studies.

1.6.1 The Internal bond angle coordinate

Changes of bond length and bond angles are among most convenient choice to define $3N - 6$ internal coordinates which are invariant under molecular translational and rotational motions. Extensive work has been reported in the literature to study vibrational spectra of triatomic and tetra atomic [18, 41, 50, 97–102] in this coordinate system. These internal coordinates follow, almost exactly, the way a molecule vibrates, i.e. elongations of bond lengths (stretching) and angular motion between them (bending). As a consequence, even a lower order Taylor expansion in potential energy is adequate for the description of molecular vibrations in comparison to Cartesian coordinates. However, the kinetic energy term is very complicated in these coordinates. Handy and Sutcliffe

[99] proposed a straightforward way to write the kinetic energy terms. They started from the kinetic energy expressed in the Cartesian coordinates and transformed it into internal coordinates by using chain rules. This transformation is carried out by expressing the Euler angles and internal coordinates as functions of the Cartesian coordinates. However, these algebraic transformations are cubersome and are restricted to only tri-atomic and tetra-atomic molecules.

1.6.2 The Local-mode coordinates

A more accurate coordinate system to describe the high energy vibrations is the local mode coordinates [50, 103–111]. The highly excited vibrational states, particularly overtones of OH and CH stretching can be treated as localized oscillators. This means that the diagonal anharmonic terms exceeds the non-diagonal inter-mode coupling strengths. In the normal mode description, the non-diagonal coupling terms prevail in the high excited range and as a result it gives poor description in this region. In local mode description one uses the Morse potential as potential energy function. The resultant Hamiltonian in this coordinate system is simpler and describes specific mode of vibrations ensuring that the diagonal anharmonic terms exceed over non-diagonal terms. The local-mode coordinates are well suited for overtones spectroscopy, in particularly, the stretching overtones.

1.6.3 The Jacobi coordinates

The Jacobi coordinate system [47, 50, 112–116, 127] was originally developed in the context of scattering theory [50]. In this coordinate system, the coordinates of all nuclei are defined with respect to a single central nucleus. A Jacobi vector describes the position of a given nucleus with respect to center of mass of a set of nuclei. The coordinate system is an obvious choice for studying large-amplitude vibrations, especially when there is more than one minimum in the potential energy surface.

1.6.4 The rectilinear Normal coordinates

Although the curvilinear coordinates offer the advantage to describe the molecular vibrations accurately over wide range of spectrum, their applications are still limited to small molecules, in particular tri-atomic and tetra atomic molecules. The main difficulty with these coordinates is that writing a generalized vibrational Hamiltonian is not possible. On the other hand this advantage is offered by rectilinear coordinates.

The definition of the normal coordinates [2–6, 16, 17, 50, 117–123] is based on the Eckart's frame. These coordinates are the linear combinations of displacement coordinates (ρ_i defined in the Eckart's frame)

$$Q_k = \sum_{i=1}^{N} \sqrt{m_i} l_{ki} \rho_i \quad i = 1, 2, \ldots, N \quad and \quad k = 1, 2, \ldots, 3N - 6. \quad (1.16)$$

l_{ik} are the elements of transformation matrix. The transformation matrix is defined in such a manner that the Hessian matrix of the molecule in these transformed coordinates is diagonal. The transformation is orthogonal by virtue of the relation

$$\sum_{i=1}^{N} l_{ij}^{T} l_{ik} = \delta_{jk} \qquad j, k = 1, 2, \ldots, 3N - 6. \quad (1.17)$$

Following the Eckart's conditions, the transformation matrix satisfies the relations,

$$\sum_{i=1}^{N} \sqrt{m_i} l_{ik} = 0 \qquad and \qquad \sum_{i=1}^{N} \sqrt{m_i} z_i^0 \times l_{ik} = 0. \quad (1.18)$$

Watson [20, 122] derived a simple form of vibrational Hamiltonian in normal coordinates following the work of Eckart [16], Wilson and Howard [117, 122], Darling and Dennison [123], Amat and co-workers [119, 120]. The Watsonian Hamiltonian is written as,

$$\hat{H} = \sum_{\alpha,\beta} \frac{1}{2} \hbar (\hat{J}_\alpha - \hat{\pi}_\alpha) \mu_{\alpha\beta} (\hat{J}_\beta - \hat{\pi}_\beta) + \frac{1}{2} \sum_i \hat{P}_i^2 + V(Q) + U. \quad (1.19)$$

Here, α and β denote the x, y and z components of the Cartesian coordinates and $\hat{J}_\alpha$ is the αth component of total angular momentum in $\hbar$ unit. μ denotes the reciprocal of

effective moment of inertia. $V(Q)$ is the potential energy function. It can be written as a Taylor series expansion in normal coordinates,

$$V(Q) = \sum_i f_{ii}Q_i^2 + \sum_{i<j<k} f_{ijk}Q_iQ_jQ_k + \sum_{i<j<k<l} f_{ijkl}Q_iQ_jQ_kQ_l + \ldots, \qquad (1.20)$$

where, $\hat{\pi}_\alpha$ is the component of the vibrational angular momentum operator along the rotating direction α. The expression of $\hat{\pi}_\alpha$ is given by,

$$\hat{\pi}_\alpha = \sum_{i<j} \xi_{ij}^{(\alpha)}(Q_iP_j - P_iQ_j), \qquad (1.21)$$

where, ξ_{ij}'s Coriolis coupling terms [5, 9] which are obtained from the normal mode eigenvectors of the potential energy function. U is a mass dependent term known as Watson term and is given by

$$U = -\left(\frac{\hbar^2}{8}\right) \sum_\alpha \mu_{\alpha\alpha} \qquad (1.22)$$

If the Taylor series expansion of Eq. 1.20 is truncated after quadratic term and Coriolis coupling and Watson terms are neglected then the vibrational Hamiltonian in Eq. 1.19 becomes the sum of one mode harmonic oscillator Hamiltonians

$$H_0 = \frac{1}{2}\sum_i \hat{P}_i^2 + \sum_i \omega_i Q_i^2 = \sum_i h(i) \qquad (1.23)$$

where, ω_i is the harmonic frequency of ith mode. Since Schrödinger equation associated with harmonic oscillator is exactly solvable, the Eq. 1.23 provides a good zeroth order Hamiltonian to apply variational or perturbative methods for anharmonic vibrational studies.

1.7   Methods to solve Vibrational Schrödinger Equation:

Like other branches of quantum many-body systems, mainly two different type of approaches are evolved to solve the Schrödinger equation associated with molecular vibrations. One is based on variational principle [7, 9, 21, 24] and other one is based on perturbation theory [7, 9, 22]. The vibrational configuration interaction method (VCI)

[32, 38–42, 126, 127, 130], vibrational self consistence field theory (VSCF) [25–32] etc belong to the formal class. On the other hand within perturbative approach, Moller-Plesset (VMP) [53–59] and canonical van Vleck perturbation (CVPT) [47–52] methods are developed and applied extensively.

1.7.1 Vibrational self-consistent field theory

The most common approximation to solve the quantum many-body problem is based on *mean field approach*. In this approach the many-body problem is decomposed to a set of coupled one body problem. The well known *Hartree-Fock* method or *Self-consistent field method* (SCF) [21, 92] is widely applied for the description of atomic and molecular electronic structure and nuclear structure. The SCF method was first introduced to calculate vibrational energy levels by Carney *et.al.* [25] followed by many other authors [26–33]. In this method, each mode of vibration is considered within a effective mean field potential generated by other modes.

In VSCF, a product of single-mode wave functions (conventionally called modal)

$$\Psi_{n_1,n_2,...n_m} = \prod_{j=1}^{m} \phi_j^{(n_j)}(Q_j) \tag{1.24}$$

is taken as trial function and the energy expectation value is minimized with respect to these single-mode functions.

$$\delta \frac{\langle \Psi_n | H | \Psi_n \rangle}{\phi_j^{n_j}(Q_j)} = 0. \tag{1.25}$$

In this way, one obtains a set of integro-differential equations

$$[h(i) + \langle \prod_{j \neq i}^{m} \phi_j^{n_j} | V_c | \prod_{j \neq i}^{m} \phi_j^{n_j} \rangle] \phi_i^{n_i} = \varepsilon_{n_i} \phi_i^{n_i}. \tag{1.26}$$

These coupled equations are solved iteratively to get optimized single-mode function and energies. The total energy is given by,

$$E_n = \sum_{j=1}^{m} \varepsilon_j^{(n)} - (N - 1) \times [\langle \prod_{j \neq i}^{m} \phi_j^{n_j} | V_c | \prod_{j \neq i}^{m} \phi_j^{n_j} \rangle]]. \tag{1.27}$$

12

The last term is due to double counting on off-diagonal interaction in the potential. Eq. 1.26 can be solved both numerically and algebraically. In algebraic solutions, one expands each single-mode function in terms of linear combination of d_i orthogonal harmonic oscillator or non-orthogonal distributed Gaussian basis functions

$$|\phi_i^{n_i}\rangle = \sum_{\nu}^{d_i} C_{\nu i}^{n_i} |\chi_\nu\rangle. \tag{1.28}$$

Each equation in Eq. 1.26 takes a matrix form. These matrices are iteratively diagonalized until converged. Finally, one gets d_i solutions $\{\phi_i^{n_i}\}$ for each of $3N - 6$ modes. Among these d_i modals, the lowest energy modal is called occupied and rest are called virtual modals.

The VSCF method involves replacement of the complicated many-body problem by an effective one body problem in which the interactions of vibrational modes are taken in an average manner. Due to single-mode nature of the effective potential, the VSCF does not account the correlation effects, i.e. nonseparability of true vibrational wave functions. This correlation error can be very large when the mode couplings are strong. This leads to the formulation of methodologies like VSCF-CI, vibrational multi-configurational self-consistent field method.

1.7.2 Vibrational Configuration Interaction method

The *vibrational configuration interaction* (VCI) method is conceptually the simplest method to solve vibrational eigenvalue equation. It requires formation and diagonalization of the vibrational Hamiltonian matrix in a configurational space. There are two ways to construct the vibrational Hamitonian matrix. One uses the optimized VSCF basis functions to generate the configurations and the Hamiltonian matrix is generated using these configurations. This is similar to CI method in electronic structure theory [21, 93] and referred as VSCF-CI method [32, 38–42]. The second method uses the values of the wave function at N discrete grid points using continuous polynomial functions. The

Hamiltonian matrix is constructed in these grid points. This method is referred as the *discrete variable representation* (DVR)[126, 127, 130–133, 138] method.

The algebraic solution of the VSCF equations provides a basis set $\{\phi_i\}$ to perform VCI calculation. The configurations are generated by replacing the occupied modals with the virtual modals of same mode. The VCI wave function is written as a linear combination of these configurations.

$$\Psi_n^{VCI} = \sum_m C_{mn} \Psi_m^{VSCF}. \tag{1.29}$$

The linear variation principle is used to determine the co-efficient C_{mn}. This is equivalent to diagonalize the VCI matrix

$$H_{mn} = \langle \Psi_m^{VSCF} | H | \Psi_n^{VSCF} \rangle, \tag{1.30}$$

to obtain eigenvectors and eigenvalues.

Romanowski *et. al.* [28] explored the idea of using basis set of eigenfunctions of the uncoupled anharmonic oscillator (UAO) Hamiltonian

$$h_k^0 = \frac{1}{2}\hat{P}_k + \omega_k Q_k^2 + f_{kkk} Q_k^3 + f_{kkkk} Q_k^4 \tag{1.31}$$

to construct configurations in VCI calculation. It is found that both UAO-CI and SCF-CI energies are roughly equal for a given basis set.

The VCI is in principle an exact method. However, the dimension of VCI matrix increases exponentially with the number of vibrational degrees of freedom which makes full VCI practically inapplicable for large molecules. So, for practical purpose one has to truncate the expansion of the VCI wave function. This truncation is not straight forward as in case of electronic structure theory. The two body nature of the electronic Hamiltonian ensures that CISD is the best truncation scheme in terms of accuracy. In case of molecular vibration, since the Hamiltonian contains more than two body terms, the triple and quadruple excitations are also significant in terms of accuracy. Several authors used the Davidson's iterative diagonalization scheme [96] to compute few lower

lying eigenvalues and eigenvectors of VCI matrix [43, 45]. This method bypasses the need of complete diagonalization of full VCI matrix by using matrix-vector product of the Hamiltonian with a trial vector.

Apart from the large configurational space problem, truncated VCI is not able to satisfy two most important criterias namely the *size consistency* and the *size extensivity* [93].The size consistency signifies the proper description at dissociation limit and size-extensivity is related to the proper scaling of energy with respect to the size of the system. These two concepts are discussed in details in the next section.

1.7.3 Vibrational multi-configurational SCF method

The *multi-configurational self consistent field theory* (MCSCF) [94] is a more accurate alternative to the traditional truncated CI method. The basic idea of this approach is to use the variation principle to determine the single particle functions that are used in the CI expansion. Following its wide implementations to molecular electronic structure theory, Culot and Liévin introduced [34, 35] the method to molecular vibrational calculations. The vibrational wave function in this case is written as

$$\Psi_{VMCSCF} = \sum_i C_i \Psi_i,$$ (1.32)

where, Ψ_i is a single-product of one mode harmonic oscillator functions represent a vibrational configuration which can be obtained from a VSCF calculation. In VMCSCF procedure, both the expansion coefficient C_i and one mode basis functions in Ψ_i are optimized. Culot and Liévin proposed a solution based on the *generalized Brillouin theorem* (GBT) which states that the Hamiltonian matrix elements between a self-consistent wave function and single excitations are zero.

$$\langle \Psi_{VMCSCF} | H_{vib} | \Psi_{kl}^\nu \rangle = 0.$$ (1.33)

Here, Ψ_{kl}^ν denotes a single excited multiconfigurational function obtain by replacing the state k by state l of the mode ν. Thus the VMCSCF method involves two step solutions.

In the first step, one solves the linear variational problem with the wave function in Eq. 1.32 to get the configuration functions and in the second step one solves Eq. 1.33 to ensure that the configuration functions satisfy the GBT.

The MCSCF method, however, involves the manual choice of the configurations space for the wave function expansion which requires a prior knowledge about the system. Essentially, a SCF calculation decides which configurations to be used for the MCSCF wave function. A more general extension to MCSCF methodology is the *complete active space SCF* method [95]. Here, a set of single space functions (modals in case of molecular vibrations) determine so-called active space. The multi-configurational wave function is expanded as linear combination of all the configurations generated out of these active space. The *vibrational complete active space SCF* method (VCASCF) has been formulated by Culot and Liévin [35]. They defined the active space in terms of all functions in a given mode up to a specific vibrational quantum number. It is found that VCASSCF provides better convergence in comparison to VMCSCF.

Recently Rauhut and co-workers proposed a different methodology to solve the VMCSCF problem based on Hermicity condition to optimize the modals [36]. Both a polynomial or a grid representation of the Hamiltonian are used by the authors. This method is very much like Fourier grid Hamiltonian multiconfiguration method [37] developed by Webb and Hammes-Schiffer in order to calculate hydrogen nuclear wave functions in quantum/classical molecular dynamics simulations of hydrogen transfer reactions.

1.7.4 DVR approach

One of the most elegant and powerful variational method to solve the vibrational eigenvalue equation is *discrete variable representation* (DVR) method [125–143]. In the general variational methods in quantum problem the trial wave function of any bound system is written as a linear combination of known complete set (infinite) of orthogonal discrete basis functions. This basis set is truncated up to a finite limit and the eigenvalues of the Hamiltonian is variationally optimized in this truncated basis set representation. In DVR

this truncated basis set representation is transformed into a representation of continuous functions that are localized (in a limited sense) on a grid in coordinate space. This transformation can be obtained using appropriate numerical quadrature (for example Gaussian quadrature).

The DVR is introduced to chemical physics literature by Harris et. al [124]. These authors showed that the eigenvalues of the coordinate matrix generates the transformation for DVR. They used harmonic oscillator basis functions to construct the matrix for coordinates. Dickinson and Certain [126] showed that these eigenvalues are equivalent to Gaussian quadrature points for Hermite polynomial.

The DVR is extensively used in the rotation-vibration literature by many authors [133–143]. In this method, one generates the ro-vibrational Hamiltonian matrix by using appropriate polynomial function and numeric quadrature. This Hamiltonian matrix is diagonalized to obtain the vibrational energy and eigenvectors. There are many possibilities to construct the DVR Hamiltonian depending on the choice of the polynomial and numerical quadratures. Bačič, Light [130] and many other authors used a distributed Gaussian basis to generate the DVR which is referred as DGB-DVR. Among others, Manolopoulos and Wyatt used Lobatto quadrature and functions (Lobatto DVR) [131], Colbert and Miller used Chebyshev polynomial and Gaussian quadrature to construct the DVR (Sinc DVR) [132].

Using the same transformation one can obtain an orthogonal discrete basis set to represent the Hamiltonian matrix that contain exactly same approximation as the DVR. This representation is referred as *finite basis representation* (FBR) [125, 137]. The kinetic energy becomes simpler in this representation and is determined by numerical quadrature over the DVR points.

There are mainly two advantages of using DVR. First, in this representation the coordinate operator is diagonal and consequently it bypasses the evaluations of integrals which is essential for general variational methods. Secondly, the Hamiltonian matrix

generated in DVR is a sparse matrix and can be efficiently diagonalized. Several diagonalization methods e.g. the Lanczos algorithm[134], the recursive residue generation method [129], Fourier-Lanczos method [135] have been used by different authors. It is found that among these method the most efficient is the Lanczos method [134]. It allows diagonalization of very large matrix without storing the matrix as a whole.

Carrington and coworkers introduce an efficient and accurate DVR approach called *potential optimized DVR* (PODVR) [136]. Here, the DVR is obtained from the basis set of eigenfunctions of one dimensional Hamiltonian. The kinetic energy term becomes simpler in the PODVR. Obviously the PODVR is well suited for the system where the inter-mode coupling strength is week.

1.7.5 Vibrational Perturbation Method

The perturbation theory has been one of the most powerful method to solve quantum many body problem. It has wide range of applications in calculating anharmonic molecular spectra over the years. Among many different types of perturbative approaches developed in the literature of quantum many body theory (e.g. Rayleigh-Schrödinger (RSPT) [21, 83], Brillouins-Wigner (BWPT) [83], Van Vleck (CVPT) [86]), the RSPT is conceptually the simplest one. Here, the Hamiltonian is divided into two parts: a zeroth order Hamiltonian, H_0, and small perturbation V. The complete set of eigenfunctions $\{\Psi_i^0\}$ and eigenvalues E_i^0 of H_0 are known from a previous calculation. One improves these eigenfunctions and eigenvalues systematically to eigenfunctions and eigenvalues of original Hamiltonian. So, the exact Hamiltonian is written as,

$$H = H_0 + \lambda V, \tag{1.34}$$

where, λ is a parameter that takes the zeroth order Hamiltonian to the exact Hamiltonian. In other words, $\lambda = 0$ corresponds to zeroth order Hamiltonian and $\lambda = 1$ corresponds to exact Hamiltonian. Since Hamiltonian is dependent of λ, both eigenfunctions and

eigenvalues are also dependent on λ

$$\Psi_n = \Psi_n(\lambda, Q) \qquad and \qquad E_n = E_n(\lambda, Q)$$

The exact eigenfunctions and eigenvalues of a non-degenerate state are expanded as Taylor series expansions around $\lambda=0$

$$\Psi_i = \Psi_i^0 + \lambda\Psi_i^1 + \frac{\lambda^2}{2!}\Psi_i^2 + \frac{\lambda^3}{3!}\Psi_i^3 + \dots \qquad (1.35)$$

$$E_i = E_i^0 + \lambda E_i^1 + \frac{\lambda^2}{2!}E_i^2 + \frac{\lambda^3}{3!}E_i^3 + \dots \qquad (1.36)$$

Substituting the expressions of H, Ψ_i and E_i in the corresponding Schrödinger equation and equating the co-efficients of λ one gets the perturbation corrections to energy order by order as

$$E_i^1 = \langle\Psi_i^0|V|\Psi_i^0\rangle, \qquad (1.37)$$

$$E_i^2 = \sum_{n \neq i} \frac{\langle\Psi_i^0|V|\Psi_n^0\rangle\langle\Psi_n^0|V|\Psi_i^0\rangle}{E_i^{(0)} - E_n^{(0)}}. \qquad (1.38)$$

The efficiency and convergence of the perturbation series depends on the choice of zeroth order Hamiltonian H_0. If H_0 is chosen wisely and V is very small then perturbation series converges quickly. One choice of zeroth order Hamiltonian is sum of one mode harmonic oscillator Hamiltonians. In this case the anharmonic force field is perturbation. There are some earlier studies based on this kind of partitioning.

Norris *et. al.* [58] and Gerber and coworkers [53–55] introduced Møller-Plesset partitioning scheme [23] in the same spirit of electronic structure theory [21]. In this scheme, the zeroth order Hamiltonian is the sum of effective one mode Hamiltonian from VSCF calculation, i.e. the perturbation operator is $V = H - \sum_i h_i^{vscf}$. It is well known that the first order correction to correlation energy is zero as a consequence of Brillouin's theorem. The vibrational second order Møller-Plesset (VMP2) correction is obtained from Eq. 1.38. The second order corrections to VSCF is termed as *correlation-corrected VSCF* (cc-VSCF) by Gerber and co-workers [53–55] and successfully applied to several systems.

The VMP2 expression in Eq. 1.38 assumes that the zeroth order energies are well separated. In case of degeneracy or near degeneracy in the eigen spectrum of zeroth order Hamiltonian, the second order energy expression blows up because of very small value of the denominator. This kind of situation is very common in case of molecular vibrations. For example, frequency of bending mode involving H atoms is about half of its stretching mode. These two modes can strongly mix with each other through 2:1 resonance (so-called Fermi resonance). Like these, other kind of resonances e.g. Darling-Dennison resonance (2:2) are also very frequent. These lead to instability of perturbative solutions. Matsunaga *et.al* [59] proposed *vibrational degenerate perturbation theory* to handle this near degeneracy problem. They expanded the k-fold degenerate wave function as linear combination of the degenerate zeroth order functions obtained from VSCF calculation,

$$\Psi_i^0 = \sum_{j=1}^{k} C_{ij}\phi_j.$$ (1.39)

Substitution of this Ψ_i^0 to the first order energy expression results a set of k simultaneous linear equations. This is equivalent to a CI problem in the space spanned by k degenerate subspaces. The eigenvalues obtain by diagonalizing the perturbation Hamiltonian V in this space are referred to as DPT1-VSCF. Similar way one can obtain the second order energy expression as

$$E_i^2 = \sum_{n \neq n'} \frac{\langle \phi_{n'}|V|\Psi_n^0 \rangle \langle \Psi_n^0|V|\phi_{n'} \rangle}{E_i^0 - E_n^0}.$$ (1.40)

The VSCF energy corrected up to second order using the degenerate perturbation theory is referred as DPT2-VSCF.

1.7.6 Canonical Van Vleck Perturbation Theory:

The canonical Van Vleck perturbation theory (CVPT) [84–90] is an attractive alternative for the description of quantum many body systems. It was first formulated by Shavitt and Redmon [84] in the context of degenerate perturbation theory in electronic structure calculation. The idea of Van Vleck perturbation perturbation theory is to transform the

Hamiltonian in to a effective Hamiltonian via unitary transformation

$$K = U^{-1}HU. \tag{1.41}$$

The solutions of the effective Hamiltonian can be obtained using a significantly smaller basis set (model space) than is needed to obtain the solutions of the original Hamiltonian. Shavitt and Redmon used exponential form of the operator U as

$$U = e^G, \tag{1.42}$$

where, G is an anti-Hermitian operator, i.e. $G = -G$ and has no diagonal component. They used super-operator framework developed by Primas [85] in their CVPT formalism. The advantage of this approach is that the theory can be completely formulated in the domain of Lie algebra.

Following the sucess of CVPT in electronic structure theory, Sibert and co-workers [47–51, 112] introduced the methodology to describe molecular vibrational spectra. Sibert started from the Nielson Hamiltonian

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \tag{1.43}$$

as the starting point of CVPT formulation. Here λ is the perturbation parameter. The zeroth order Hamiltonian $H^{(0)}$ is the sum of the Harmonic oscillator Hamiltonian corresponds to different modes of vibrations:

$$H^{(0)} = \frac{1}{2} \sum_{i=1}^{N} P_i^2 + \omega_i^2 q_i^2. \tag{1.44}$$

where, ω_i is the harmonic frequency and q_i is the vibrational coordinate (say, normal coordinate) of the i'th mode.

While Shavitt and Redmon determined the effective Hamiltonian K order by order, Sibert used a series of unitary transformations to the original Hamiltonian to obtain the

effective Hamiltonian,

$$K_1 = exp(i\lambda^1 S^{(1)}) H exp(-i\lambda^1 S^{(1)}) \tag{1.45a}$$

$$K_2 = exp(i\lambda^1 S^{(2)}) K_1 exp(-i\lambda^1 S^{(2)}) \tag{1.45b}$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$$

$$K = exp(i\lambda^1 S^{(n)}) K_n exp(-i\lambda^1 S^{(n)}). \tag{1.45c}$$

One first calculates K_1, then K_2 and so forth. The computational procedures to obtain these transformations are same. K_1 is determined by using the well known Hausdorff formula,

$$K_1 = H + i\lambda[S^{(1)}, H] - \frac{\lambda^2}{2!}[S^{(1)}, [S^{(1)}, H]] + \dots. \tag{1.46}$$

and expanding H and K in terms of powers of λ. Equating the powers of λ one gets the expressions of each order as K_1

$$
\begin{aligned}
K_1^{(0)} &= H^{(0)}, \\
K_1^{(1)} &= H^{(1)} + i[S^{(1)}, H^{(0)}], \\
K_1^{(2)} &= H^{(2)} + i[S^{(1)}, H^{(1)}] - \frac{1}{2!}[S^{(1)}[S^{(1)}, H^{(0)}],
\end{aligned}
\tag{1.47}
$$

and so on.

The perturbative Hamiltonian $H^{(1)}$, $H^{(2)}$ etc are rewritten in terms of harmonic oscillator ladder operators. For example,

$$H^{(1)} = \sum_m \sum_n \prod_{j=1}^{N} (a_j^\dagger)^{m_j} (a_j)^{m_j}. \tag{1.48}$$

The choice of the canonical operator S determines the form of the effective Hamiltonian. For example, a choice of

$$S^{(1)} = {\sum_m}' {\sum_n}' \prod_{j=1}^{N} (a_j^\dagger)^{m_j} (a_j)^{m_j} \tag{1.49}$$

leads to

$$K_1^{(1)} = \sum_m{}'' \sum_n{}'' \prod_{j=1}^{N} (a_j^\dagger)^{m_j} (a_j)^{m_j}, \qquad (1.50)$$

where, $\sum = \sum' + \sum''$.

The most attractive feature of the CVPT is that it gives the flexibility in choosing S. For a given choice of $S^{(1)}$ the perturbation corrections to the effective Hamiltonian can be defined from Eq. 1.47. K_2, K_3 etc are also determined order by order in the same manner.

As stated earlier, the occurrence of degeneracy or near-degeneracy in the vibrational eigenvalue spectroscopy is very frequent due to large mismatch between zeroth order energies of the stretching and bending mode. This leads to divergence in the perturbation expansion. Sibert and co-workers used almost degenerate perturbation theory [48] to account this problem. Here, one chooses $S^{(i)}$ in such a way that it includes all terms except those which satisfy the relation

$$\sum_{i=1}^{N} c_i(m_i - n_i) = 0. \qquad (1.51)$$

The value of c_i is decided from the previous knowledge of the molecule. For example, in case of H_2CO, $c_i = 2$ for all four stretching modes and $c_i = 1$ for the bending modes. The effective Hamiltonian K generated this way is block diagonal within a given symmetry block. The solution of the effective Hamiltonian can be obtained with greatly reduced basis sets.

Sibert's CVPT formalism has been used extensively to describe the molecular vibrations in both curvilinear and rectilinear normal coordinate systems. The results are found to be highly accurate. Recently, Dawes and Carrington [52] used second order CVPT to obtain effective one-dimensional basis functions in multi-dimensional vibrational problems.

Recently, Yagi *et.al.* [91] developed *quasi-degenerate perturbation theory* (QDTP) based on Shavitt and Redmon formalism of Van Vleck perturbation theory. The quasi-degenerate functions in model space are obtained from VSCF calculation. In this respect

this approach is similar to degenerate perturbation theory by Matsunaga *et.al.* [59] described in the earlier subsection. While Sibert's approach uses a previous knowledge of the system to treat the degeneracy, the QDTP is based on automatic generation of quasi-degenerate model space.

1.8 Size consistency and size extensivity

As stated earlier, any approximate many body method should satisfy two important criteria, namely size consistency and size extensivity [21, 144–146]. As defined by Pople and co-workers [144], a method is size consistent if energy of a molecule is the sum of energies of its fragments at non-interacting limit. In other words, if a system has N non-interacting monomers with energy e_i, its total energy will be Ne_i. This means, if a system consists of two non-interacting fragment A and B, (or if AB molecule dissociates in to A and B at infinite separation) then the energy should be additively separable

$$E_{AB} = E_A + E_B, \tag{1.52}$$

and the wave function should be multiplicatively separable

$$\Psi_{AB} = \Psi_A \Psi_B. \tag{1.53}$$

The concept of size extensivity is related to size consistency. It accounts proper scaling of the energy with the number of particle i.e. with the size of the system. Unlike size consistency, which is a property of infinite separation of the fragments of the system, size extensivity is a more general mathematical concept that hold at any situation. If a method is not size extensive, the error in calculated energy will scale as N^m, where m is either less than 1 or greater than 1 and N is the number of particles present in the system. In the former case, the correlation energy per particle decreases as the number of particle N increases and becomes zero as $N \rightarrow \infty$. In the later case, the correlation energy per particle becomes infinity as $N \rightarrow \infty$. Therefore, it results unphysical behavior in energy calculations. It is well studied in the context of electronic structure theory that any

truncated CI calculation does not satisfy these two properties. It can be easily shown that the wave functions obtained from any truncated CI calculations are not multiplicatively separable and hence the energies of the fragments are not additively separable. It holds in the case of vibrational calculations also.

1.9 The method of second quantization and the Diagrammatic techniques:

The method of second quantization and diagrammatic techniques [147–153] of quantum field theory offers more simpler formulation of quantum many body theories than the traditional route. Historically, the second quantization was first introduced by Dirac in his treatment of quantization of radiation field [148]. The idea is extended to many body methods like Green function theory[21, 151, 152], Many body perturbation theory [21, 151, 152], Coupled cluster method [60–64, 189, 190] for the description of fermion and bosonic systems over last few decades.

In the second quantization, many particle wave function and operators are represented in terms of creation and annihilation operators. A creation operator $a_i^\dagger$ creates a particle on single particle state $|i\rangle$ and an annihilation operator a_i annihilates a particle from the single particle state $|i\rangle$. So, if a creation operator acts on a N particle symmetric (in case of bosons) or anti-symmetric (in case of fermions) function it generates a (N+1) particle symmetric or anti-symmetric function respectively

$$a_i^\dagger |jk...l\rangle = |jk..li\rangle p. \tag{1.54}$$

Here p is the phase acquired by the wave function during this process. Similarly one annihilation operator generates (N-1) particle function from N particle function by its action

$$a_i |ijk...l\rangle = |jk..l\rangle p. \tag{1.55}$$

In the case of fermion systems, since one orbital cannot be occupied by more than one

particle, the action of a creation operator on a many particle system is zero if the orbital is already present in the many particle function. If the one particle basis set is chosen to be orthogonal then the creation and annihilation operators are adjoint to each other, i.e. $(a_i^\dagger)^\dagger = a_i$. The symmetry requirements of many body functions for indistinguishable particles is inherently built in the commutation/anti-commutation relations of the creation and annihilation operators,

$$[a_i^\dagger, a_j^\dagger]_\pm = 0 \tag{1.56a}$$

$$[a_i, a_j]_\pm = 0 \tag{1.56b}$$

$$[a_i, a_j^\dagger]_\pm = \delta_{ij} \tag{1.56c}$$

where, '$-$' sign signifies commutation relation applicable for boson particles and '$+$' signifies anti-commutation relation applicable for fermion system.

In addition to these creation and annihilation operators, it is necessary to define a vacuum state for the formulation of second quantization. A vacuum $|0\rangle$ is a normalized state with no particle in it. The vacuum state is purely a mathematical concept having following properties.

$$a_i^\dagger|0\rangle = |i\rangle \tag{1.57}$$

$$a_i|0\rangle = 0 = \langle 0|a_i^\dagger \tag{1.58}$$

$$\langle 0|0\rangle = 1 \tag{1.59}$$

The first equation signifies that the creation operator acting on zero particle Hilbert space generates one particle Hilbert space. Similarly, the many body function of any number of particle can be generated by the successive operation of the creation operators on the vacuum state

$$a_i^\dagger a_j^\dagger .....a_l^\dagger|0\rangle = |ij...l\rangle. \tag{1.60}$$

So, the creation operators $a_i^\dagger$ do not operate only on a single Hilbert space, rather it operates on one Hilbert space and generates another Hilbert space. The direct sum of all

these Hilbert spaces form another linear vector space called the Fock space [151, 152]

$$B = B_0 + B_1 + B_2 + \ldots \ldots = \oplus_{n=0}^{\infty} B_n \qquad \text{for bosons.} \qquad (1.61a)$$

$$F = F_0 + F_1 + F_2 + \ldots \ldots = \oplus_{n=0}^{\infty} F_n \qquad \text{for fermions.} \qquad (1.61b)$$

An operator expressed in the second quantization notations does not depend on the number of particle of the system. The expectation values of such operator between two functions of a Fock space are easily determined by applying the concept of normal ordering and *generalized Wick's theorem* [152, 155]. The *generalized Wick's theorem* states that any time order operator string can be written as normal ordered form plus sum of all possible contractions. A sequence of creation and annihilation operator is said to be normal ordered if all annihilation operators are placed at the right of the creation operators. When a commutation/anti-commutation is performed between a pair of creation and annihilation operators, two terms arise. One that does not contain the pair of creation-annihilation operators is known as contraction term. In the second term the creation and annihilation operator pair is commuted/anti-commuted. The states of the many particle system between which the expectation values to be calculated are written as a string of annihilation/creation operators acting on the vacuum. By applying the generalized Wick's theorem, this sequence of operator is written as normal ordered form and sum of all possible pair of contractions. Since the expectation values of the normal ordered operators over the vacuum state are zero, the matrix elements will survive only when the creation and annihilation operators are fully contracted.

The diagrammatic representation of the Wick theorem bypasses the cubersome algebraic formulations of the many body methods. The diagrammatic techniques was first introduced by Feynman [154] in the context of quantum field theory and later on successfully applied to many electron problem [149, 150, 190]. The above described correlation methods e.g. configurational interaction, many body perturbation theory etc are re-expressed in terms of second quantization. The diagrammatic representations of

the corresponding energy terms and amplitude equations not only simplify the formulation but monitor the size extensivity. For example, in second quantization, the CI wave function can be rewritten by a wave operator operating on a vacuum defined by a non-interacting many body function

$$|\Psi\rangle = (1 + \hat{C})|\Phi_0\rangle, \tag{1.62}$$

with,

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \ldots. \tag{1.63}$$

Here, $\hat{C}_1$, $\hat{C}_2$ etc are the one body, two body excitation operators that generate the configurations by their action on the vacuum. Substituting this wave function ansatz in the Schrödinger equations followed by projecting various configuration functions, one gets the following equations for CI

$$\langle\Phi_0|\hat{H}_N(1 + \hat{C})|\Phi_0\rangle = E_{corr} \tag{1.64a}$$

$$\langle\Phi^*|\hat{H}_N(1 + \hat{C})|\Phi_0\rangle = E_{corr}\langle\Phi^*|\hat{C}|\Phi_0\rangle \tag{1.64b}$$

where, $\hat{H}_N$ is the normal ordered form of the Hamiltonian and $\langle\Phi^*|$ are the excited configurations. All these matrix elements in these equations can be evaluated using generalized Wick's theorem. The correlation energy E_{corr} is size extensive if its diagrammatic representation contains only connected closed diagrams. Due to presence of the E_{corr} term at the right hand side of the amplitude equations, it generates some disconnected diagrams. Such disconnected diagrams have parts which are closed and connected. This type of diagrams are referred as unlinked diagrams. These unlinked diagrams are responsible for the size-inextensivity.

In case of RSPT, these unlinked terms appear beyond second order in the energy expression. Bruckner algebraically [156] and Goldstone and Hugenholtz diagrammatically [157] showed that these unlinked terms in RSPT cancel each other within each perturbative order. This result is known as *linked cluster theorem* (LCT).

1.10 The Coupled Cluster theory

The coupled cluster method has been established as one of the most accurate techniques for the description of quantum many body system [60–67, 189, 190]. In particular, it has immense success in the description of electronic structures of atoms and molecules over last few decades. Using MBPT, Hubbard [158] showed that the exact ground state wave function of many particle system can be parametrized by an exponential wave operator operating on the zeroth order wave function. Coester and Kümmel [159] formally introduced the exponential S method or later on known as coupled cluster method by using this exponential parametrization of ground state many particle wave function in the context of nuclear physics. Later on, the idea was introduced in quantum chemistry by Cizek and Paldus [60]. However, the relevance of the cluster expansion of the wave function in electronic structures of atoms and molecules was studied by Sinanoglu [160] and Nesbet [161] from a different perspective.

The coupled cluster wave function for ground state of many body system is written as,

$$|\Psi gr\rangle = e^{\hat{T}}|\phi_0\rangle = \Omega|\phi_0\rangle. \tag{1.65}$$

The operator $\hat{T}$, known as the correlation cluster operator, is the sum of connected singles, doubles, triples, up to n-truple excitation operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots, \tag{1.66}$$

and ϕ_0 is the reference function. The action of $\hat{T}_1$, $\hat{T}_2$ etc on the reference function generates singly excited, doubly excited and so on configurations just like $\hat{C}_1$, $\hat{C}_2$ in CI method. One can easily view the relation between CI wave function and CC wave

function through following equations,

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

(1.67)

and so on.

This correspondence holds only in the exact limit. In practice, the exact CCM is never pursued simply because its nonlinear structure is much more complicated than linear expansion in full CI. However, the most attractive feature of CC wave functions is that it contains all the excited configurations in an approximate manner even at a lower order truncation of the wave operator. For example, if $\hat{T}$ contains only singly and doubly excitation operators then because of the exponential nature of the wave operator, the resultant wave function contains some of the triply excited configurations generated by $T_1 T_2$, quartic excited configurations generated by T_2^2 and T_1^4 and so on. As a consequence, it is much more accurate that the truncated CI wave function. Again due to exponential nature of the wave operator, the resultant function is multiplicatively separable at any level of truncation and hence the method is size consistent. In diagrammatic language, one can say that the higher order clusters appear in the wave function as lower order linked diagrams. This makes the CCM size extensive at any level of approximation.

The ground state energy can be obtained by projecting the reference state to the corresponding Schrödinger equation,

$$
\langle \phi_0 | \hat{H} e^{\hat{T}} | \phi_0 \rangle = E_{gr} \langle \phi_0 | e^{\hat{T}} | \phi_0 \rangle = E_{gr}.
$$

(1.68)

Here, intermediate normalization $\langle \phi_0 | \Psi_{gr} \rangle = 1$ is assumed. The equations for the cluster amplitudes are obtained by projecting the excited configurations $\langle \phi^* |$

$$
\langle \phi^* | \hat{H} e^{\hat{T}} | \phi_0 \rangle = E_{gr} \langle \phi^* | e^{\hat{T}} | \phi_0 \rangle.
$$

(1.69)

The diagrammatic representation of Eq. 1.69 is unlinked due to presence of E_{gr}. However, the diagrammatic analysis of left hand side shows that it also contains some unlinked terms due to presence of the exponential operator. The unlinked terms of both sides exactly cancel each others.

The coupled cluster equations 1.69 and 1.68 are not amenable to the practical computer implementations. The most convenient way is the use of similarity transformation technique. Pre-multiplying the corresponding Schrödinger equation by $e^{-\hat{T}}$ one obtain the following equation

$$e^{-\hat{T}} H e^{\hat{T}} |\phi_0\rangle = E_{gr} |\phi_0\rangle. \tag{1.70}$$

Upon subsequent projection of the reference $\langle\phi_0|$ state and excited configurations one can easily obtain the modified formula for energy and cluster amplitudes,

$$\langle\phi_0| e^{-\hat{T}} H e^{\hat{T}} |\phi_0\rangle = E_{gr}, \tag{1.71}$$

$$\langle\phi^*| e^{-\hat{T}} H e^{\hat{T}} |\phi_0\rangle = 0. \tag{1.72}$$

The advantage of using the similarity transformation is two fold. One, the resulting amplitude equations (1.72) are completely decoupled from the energy equation (1.71). The other is that the similarity transformation transformed Hamiltonian now can be expanded as a linear combination of nested commutators of $\hat{H}$ and cluster operator $\hat{T}$ via well known Champbell-Baker-Hausdorff (CBH) formula,

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + [[\hat{H}, \hat{T}], \hat{T}] + [[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \ldots \tag{1.73}$$

This infinite series expansion truncates naturally depending on the nature of the Hamiltonian. For example, in case of electronic structures of atoms and molecules, because of having two creation and two annihilation operators in second quantized form of the Hamiltonian, the CBH expansion truncates after the first five terms. This truncation is independent of the approximation used in $\hat{T}$ operator. The commutator structure of the equations ensure the connectedness of the diagrams.

1.10.1 Stationary Coupled Cluster Methods:

The traditional CCM, just discussed, is manifestly non-variational. However, there are some stationary approaches have been developed to solve the CC wave functions. The advantages of using the variational ansatz are on one hand, the resultant energy is upper bound and on the other hand, one can use the Hellmann-Feynman theorem and (2n+1) rule to calculate the response properties. The CC wave function $e^{\hat{T}}|\phi_0\rangle$ naturally leads to the energy functional

$$E = \frac{\langle\phi_0|e^{T^\dagger}\bar{H}e^T|\phi_0\rangle}{\langle\phi_0|e^{T^\dagger}e^T|\phi_0\rangle}. \tag{1.74}$$

This functional referred to as XCC [162–165] (expectation value coupled cluster) as it is the expectation value of the Hamiltonian. Here, $T^\dagger$ is adjoint of cluster operator T. It is the sum of one body, two body, etc de-excitation operators. However, the practical implementation of this functional is impossible because both the numerator and denominators are infinite series in $T^\dagger$ and T. Moreover, this type of functional does not explicitly exhibit the connected nature of energy as in the standard coupled cluster theory. Using linked cluster theorem, Pal *et. al.* [162, 163] showed that the numerator can be decomposed into a connected term multiplying by a disconnected term. The disconnected term exactly cancels the denominator. Therefore, the connected form of the functional,

$$E = \langle 0|e^{T^\dagger}\bar{H}e^T|0\rangle_{conn} \tag{1.75}$$

is suitable for carrying out variation. Unfortunately, this is still a infinite series even with truncations in T and $T^\dagger$ and one has to truncate for practical implementation. Various truncation schemes have been used in literature to truncate this functional. Pal *et. al.* [162, 163] used polynomial truncation based on fixed power of $T^\dagger$ and T. Bartlett and co-workers [166] used perturbative arguments for the truncation.

Alternatively, Kutzelnigg and coworkers proposed an unitary exponential ansatz of wave function for variational CCM [167],

$$|\Psi\rangle = e^\sigma|0\rangle, \tag{1.76}$$

where, $\sigma = -\sigma^\dagger$. A special choice of σ may be $\sigma = T - T^\dagger$. With this wave function the energy functional becomes,

$$E = \langle 0|e^{-\sigma}\bar{H}e^{\sigma}|0\rangle. \tag{1.77}$$

This method is referred to as unitary coupled cluster method (UCCM). This functional is connected due to BCH expansion of $e^{-\sigma}\bar{H}e^{\sigma}$ as shown in Eq. 1.73. However, the expansion leads to an infinite series and need to be truncated for practical implementations. Pal *et. al.* [162] showed that variational UCCM functional of Eq. 1.77 is identical with the connected form of the XCC functional of Eq. 1.75.

These stationary CC methods, however, were not pursued extensively due to some inherent drawbacks. One, unlike the standard variational methods, these truncated energy functional does not lead to any upper bound of calculated energy. Secondly, although the energy functional is connected, the differentiations of this functional with respect to cluster amplitudes lead to disconnected terms in the amplitude equations. Consequently, the calculated energies may not be size-extensive for specific approximations.

Arponen [168] proposed an alternate stationary coupled cluster method that uses a double similarity transformation in the energy functional

$$E = \langle \phi_0|e^{\Sigma}e^{-T}\bar{H}e^{T}e^{-\Sigma}|\phi_0\rangle. \tag{1.78}$$

Here, Σ is a de-excitation operator. This method is referred as extended coupled cluster method (ECCM) [168–170]. Basically, like ground state bra state in the traditional coupled cluster method, here ket state is also parametrized with an exponential operator,

$$\langle \Psi_0'| = \langle \phi_0|e^{\Sigma}e^{-T}, \tag{1.79a}$$

$$|\Psi_0\rangle = e^{T}e^{-\Sigma}|\phi_0\rangle. \tag{1.79b}$$

These states satisfy the bi-orthogonal relations,

$$\langle \phi_0|\Psi_0\rangle = 1, \tag{1.80a}$$

$$\langle \Psi_0'|\Psi_0\rangle = 1. \tag{1.80b}$$

The ECCM energy functional terminates naturally depending on the rank of the excitation and de-excitation operators. Arponen showed that this functional can be variationally optimized with respect to cluster operators σ and T. However, it generates some disconnected terms in the amplitude equations while differentiations leading to size-inextensivity in the energy value. Arponen [168] suggested an equivalent ansatz of type

$$E = [\langle \phi_0 | e^{\Sigma} e^{-\widetilde{T}} \bar{H} e^{\widetilde{T}} e^{-\Sigma} | \phi_0 \rangle]_{DL}, \tag{1.81}$$

for the variational calculation. Here, DL referred as double linking which means that while $\widetilde{T}$ is linked to the Hamiltonian (due to CBH expansion of $e^{-\widetilde{T}} H e^{\widetilde{T}}$), the Σ operator is connected to either at least one Hamiltonian vertex or with two separate $\widetilde{T}$ vertex. The amplitudes of T and Σ are obtain by solving the following equations respectively,

$$\frac{\partial E}{\partial \Sigma} = \frac{[\langle \phi_0 | e^{\Sigma} e^{-\widetilde{T}} \bar{H} e^{\widetilde{T}} e^{-\Sigma} | \phi_0 \rangle]_{DL}}{\partial \Sigma} = 0, \tag{1.82a}$$

$$\frac{\partial E}{\partial T} = \frac{[\langle \phi_0 | e^{\Sigma} e^{-\widetilde{T}} \bar{H} e^{\widetilde{T}} e^{-\Sigma} | \phi_0 \rangle]_{DL}}{\partial T} = 0 \tag{1.82b}$$

The DL ensures the connectedness in the T and Σ amplitudes equations.

The ECCM approach is widely used in the literature. Pal and co-workers used its double-linked variant to study the molecular properties [172, 173]. Piecuch [171] and Gordon and co-workers [174] used the method to study the molecular bond breaking. Unlike Pal and co-workers they did not use double-linked functional and instead used method of moment approach to solve Eq. 1.78. In this approach T and Σ amplitudes are decoupled from each other and their solutions are obtained sequentially.

1.10.2 Coupled cluster linear response theory:

Monkhorst [175, 176] first showed that the excitation energies can be obtained from the poles of the time-dependent coupled cluster response functions. This method is referred as *the coupled cluster linear response theory* (CCLRT). Later on, the idea was extended by many others [177–181] in several contexts. The time-independent version of linear

response theory was formulated by Mukherjee and co-workers [182]. A related time independent approach to calculate coupled cluster excited states was developed by Harris [183] using the equation of motion (EOM) formalism of Rowe [184]. Harris used an exponential operator acting on the CC ground state wave function to get the excited state wave functions,

$$\Psi_k = e^{\hat{S}} e^{\hat{T}} \Psi_0, \tag{1.83}$$

where, $\hat{S}$ is the excitation operator like $\hat{T}$. Later on, Bartlett and co-workers [185, 186] used a linear operator Ω instead of $e^{\hat{S}}$ to parametrize the excited states.

$$\Psi_k = \Omega \Psi_0 = \Omega_k e^{\hat{T}} \Psi_0, \tag{1.84}$$

$$\Omega_k = R_{k0} + R_{k1} + R_{k2} + \dots, \tag{1.85}$$

where, R_{k0}, R_{k1}, etc are CI like excitation operators. This approach is conceptually equivalent to CCLRT approach and provides same eigenvalue equations to obtain the excitation energies,

$$[\bar{H}, \Omega_k]_c |0\rangle = \omega_k \Omega_k |0\rangle. \tag{1.86}$$

Here, $\bar{H} = e^{-\hat{T}} H e^{\hat{T}}$ and $\omega_k = E_k - E_0$ is the excitation energy for k'th state. This method is known as *the coupled cluster equation of motion* (EOMCC) method from its analogy with Heisenberg equation of motion that relates a commutator to a time derivative. Solving this equation is equivalent to solving the eigenvalue equation of $\bar{H}$ (i.e. diagonalization of $\bar{H}$ in the excited manifold generated by Ω_k)

$$\bar{H} R_k = \omega_k R_k. \tag{1.87}$$

The eigenvalues ω_k are the corresponding excitation energies and R_k are the corresponding eigenvectors of the transformed Hamiltonian. The eigenvectors R_k's are connected to $\bar{H}$ because of commutator structure of Eq. 1.86. One can view the EOMCC or the CCLRT as modified CI calculation that uses a similarity transformed Hamiltonian $\bar{H}$ instead of original Hamiltonian. The similarity transformed Hamiltonian $\bar{H}$ is manifestly

a non-Hermitian operator. So, its left eigenvectors $L_k \bar{H} = \omega_k L_k$ are different from the right one and not necessarily connected to $\bar{H}$. The left and the right eigenvectors follow the bi-orthogonal relation $R_k L_l = \delta_{kl}$. Note that similar kind of parametrization for the excited states description within coupled cluster framework was used by Emrich [187] in nuclear physics. Another method proposed by Nakatsuji and Hirao [188] known as SAC-CI which is a hybrid of CC and CI method is closely related to EOMCC/CCLRT.

The CCLRT/EOMCC method is conceptually very simple and it provides a direct way to calculate the excitation energies. However, since the equations are not fully linked, the corresponding excitation energies are not size extensive. The second drawback of EOMCC method is that since it diagonalizes a non-Hermitian Hamiltonian $\bar{H}$, one may encounter complex eigenvalues in the eigenvalue spectrum. The Fock space multi-reference coupled cluster method based on effective Hamiltonian theory formulated by Mukherjee and co-workers [190, 199, 200, 202] uses a exponential ansatz to describe the excited states. It generates only the connected terms leading to size extensivity of the excited states.

1.10.3 Multi-reference coupled cluster theory:

The ground state coupled cluster is based on a single reference function. It accounts for the so-called dynamic correlations that arise due to mean field nature of the reference state in very accurate manner. However, in the cases where the reference function is degenerate or quasi-degenerate another type of correlation effect appears due to strong interactions between the reference functions. This is known as non-dynamic correlation. The *multi-reference coupled cluster method* (MRCCM) [202] has been formulated to account this non-dynamic correlation along with the dynamic correlation. The development of the MRCCM is based on the effective Hamiltonian approach [191–195] that provides a simultaneous description of a manifold of quasi-degenerate states. In this approach, the N particle Hilbert space is divided into two part: a smaller M dimensional

36

model space defined by the projection operator P

$$P = \sum_m |\phi_m\rangle\langle\phi_m|, \tag{1.88}$$

and its complimentary subspace defined by the projection operator Q. The exact target function Ψ_k assume to have a significant component Ψ_k^0 (defined by the linear combination of the reference functions of the model space) in the model space,

$$\Psi_k^0 = P\Psi_k. \tag{1.89}$$

The target exact functions are obtained by the action of a wave operator operating on the model space function

$$\Psi_k = \Omega\Psi_k^0. \tag{1.90}$$

Now, the next task of the effective operator based approach is to define the effective Hamiltonian that operates on the model space functions and give the exact energy of the target space. Two related approaches to construct the effective Hamiltonian has been widely used in the literature. In the first approach, the effective Hamiltonian is constructed by the similarity transformation of Hamiltonian through the wave operator Ω [191–195],

$$H_{eff} = \Omega^{-1}H\Omega. \tag{1.91}$$

This form of the effective Hamiltonian is applicable only when the inverse of the wave operator is exists. The second approach uses generalized Bloch equation [196]. The Bloch equation is the generalization of Schrödinger equation in the multi-dimensional space obtained by pre-multiplying the effective operator in Eq. 1.91 by wave operator Ω,

$$H\Omega P = \Omega P H_{eff} P. \tag{1.92}$$

The use of generalized Bloch equation bypasses the need of evaluation of inverse of the wave operator.

There are two kind of MRCC approaches that have been discussed in the literature depending on the choice of the wave operator Ω. In the first approach, the wave operator

is a sum of SRCC like operators defined independently for each model space function,

$$\Omega = \sum_I e^{T_I} |\phi_I\rangle\langle\phi_I|. \tag{1.93}$$

This means each function in the model space acts as vacuum and the operator T_I generates the exited configuration from the corresponding vacuum state I. This approach is first proposed by Jeziorski and Monkhorst [197] and is known as the *Hilbert-space multi-refernece coupled cluster method* (HS-MRCCM) or *state-universal multi-reference coupled cluster method* (SU-MRCCM). This approach is found to be suitable to calculate the potential energy surface of molecules.

The second approach, known as *valence universal multi-reference coupled cluster method* (VU-MRCCM), has been invoked by Mukherjee and co-workers [199–206], Lindgren [198] and Offerman and co-workers [207]. Unlike the HS-MRCC, this approach uses a common vacuum for all the reference functions in the model space. The vacuum function may correspond to a optimized state with different particle than the system of interest. The wave operator is defined as,

$$\Omega = e^T$$
$$T = \sum_{i=1}^{M} T^i, \tag{1.94}$$

is valence universal in the sense that it maps model space functions in all sectors into the exact functions. For example, in the case of calculations of electronic excitation energies of atoms and molecule, the model space is termed (1,1) sector because of having one hole and one particle in hole-particle language. The excitation operator in this case is written as,

$$T = T^{(0,0)} + T^{(0,1)} + T^{(1,0)} + T^{(1,1)}. \tag{1.95}$$

The excitation operator $T^{(0,0)}$ corresponds to (0,0) sector i.e. for vacuum, $T^{(1,0)}$ for (1,0) sector i.e. corresponds to ionized state and so on. One note that the excitation operators $T^{(0,0)}$, $T^{(1,0)}$ etc belongs to different number of particle. This approach is the *Fock-space multi-reference coupled cluster method* (FS-MRCCM). This method is

suitable to calculate excitation energies, ionization potentials and electron affinities of atoms and molecules. The details of this method will be discussed in chapter four in the context of vibrations of molecules.

1.10.4 Coupled cluster methods for property calculation:

Parallel to the calculations of energy, extensive works have been devoted to calculate the non-energetic properties within coupled cluster framework. One can categorize these properties into three classes [179]; expectation values, transition properties and response properties. In this thesis, our concern is to calculate the expectation values and transition properties. However, one can easily show that if the method is stationary then the expectation values of the operators like dipole moment etc are equal to the first order response properties [9].

Using coupled cluster wave function one can write the expectation value of any operator $\hat{O}$ as

$$\langle \hat{O} \rangle = [\langle 0|e^{T^{\dagger}} \hat{O} e^{T}|0 \rangle]_L. \tag{1.96}$$

Unfortunately, this equation leads to a non-terminating series making the ansatz inapplicable for practical implementation. Pal and co-workers [172, 173] extensively used double linked structure of extended coupled cluster method to calculate the expectation values of molecular properties. The ECCM is a stationary approach and the corresponding expectation value ansatz terminates naturally due to its double linked nature. Many authors used the response approach to calculate the expectation values within coupled cluster framework. The traditional CCM is non-variational and hence the Hellmann-Feynman theorem does not hold here. There are mainly two related approaches have been developed to eliminate the non-Hellmann-Feynman term that appear in the first order coupled cluster response. The first one is the coupled cluster Z-vector approach based on Dalgarno's interchange theorem [208]. This method was introduced by Bartlett and co-workers [209–211] following the idea of Handy and Schaefer [212] who used

the technique for analytical derivatives in CI. The second one is the constrained variational approach (CVA) [179, 181, 213, 214] based on the use of Lagrange undermined multipliers. For the calculations of first order response properties these two methods are identical.

The effective operator approach based on coupled cluster linear response theory was introduced by Prasad [215]. Here, the expectation values of the operator is calculated by using an effective operator which is a similarity transformation of the original operator $e^{-T}\hat{O}e^{T}$. The various features of this method will be discussed in chapter three.

1.11 Vibrational Coupled Cluster Method

The coupled cluster method is particularly well suited to the electronic structure theory. Here, the residual interaction is coulombic interaction which is strictly a two body operator. Second, due to Pauli's exclusion principle, the probability of three or more electrons encountering each other in a small region of space is small. These ensure that the vital part of the correlation energy comes from the two body excitation operator. Third, the energy spectrum of the unperturbed Hamiltonian is such that the n-particle excitation energy scales almost linearly with n. From perturbative arguments, this implies that the matrix elements for the n-particle cluster operator would be smaller than lower particle cluster operator because of the larger energy defects that go into the denominator. None of these conditions hold in the case of molecular vibrational problem. The residual interaction is a many body function. For semi-rigid molecules, the vibrational modes may be treated as distinguishable particles, and hence no statistics induced effects appear. Lastly, the zeroth order spectrum of the molecular vibrations corresponds to the harmonic oscillator. The energy levels of the individual modes are evenly spaced. Hence, the excitation energy for one, two...n-body excitation operators could be nearly equal. For example, the two stretching modes in H_2O molecule have similar energies (around $3000cm^{-1}$) which are almost double of its bending mode energy. As a result, the excitation energy

of two body excitation operator corresponding to the bending mode is nearly equal to one body stretching mode excitation operator. Under these conditions, it is desirable to test the applicability of the CCM to the molecular vibrations.

The construction of the Fock space is the heart of coupled cluster formalism. There are two representations possible for the construction of Fock space of vibrational coupled cluster method. The first one is the basis set method which use single mode creation and annihilation operator to construct the elements of the Fock space. This route is mainly followed by Christiansen and co-workers [72, 75–82]. The second one is the bosonic representation where simple harmonic ladder operators are used to construct the elements for Fock space [68–74]. This approach is followed by Bishop and co-workers [66], Hsue and Chern [65] and Kaulfuss and Attenbokum [67] for coupled cluster description of one dimensional anharmonic oscillators and later on by Prasad and co-workers [68–71] for the description of molecular vibrations.

1.11.1 Basis set approach in vibrational coupled cluster method

As described earlier that the coupled cluster method is a Fock space approach. It requires the construction of a Fock space and the associated operators that connect the different functions in the Fock space. In the basis set representation, one defines a single particle Hilbert space H_1^α for each mode α. All possible k particle Hilbert spaces H_k are formed as the tensor product of these single particle Hilbert spaces associated set of k modes. The Fock space is defined as the union of all such k particle Hilbert spaces. This approach was used by Latha and Prasad to describe intramolecular vibrational relaxation dynamics, and more recently, by Christiansen and co-workers to describe molecular vibrational eigenstates. The associated operator is constructed using creation/annihilation operators corresponding to each mode. For example, the creation operator $a_{r^m}^{m\dagger}$ creates a modal of corresponding m^{th} mode in the energy level r^m and $a_{r^m}^m$

annihilates the same. The creation/annihilation operators corresponding to one particular mode can not create/annihilate any modal of other mode. Again, since the vibrations in semi-rigid molecules can be treated as distinguishable particles, the order of creations or annihilation operators corresponds to different modes is irrelevant, that means $a_r^{1\dagger} a_s^{1\dagger} |vac\rangle = a_s^{1\dagger} a_r^{1\dagger} |vac\rangle$. Keeping these facts in mind one can write the commutation relations of the creation and annihilation operators as

$$[a_{r^m}^m, a_{s^{m'}}^{m'\dagger}] = \delta_{m,m'} \delta_{r^m, s^m}, \tag{1.97}$$

$$[a_{r^m}^m, a_{s^{m'}}^{m'}] = 0, \tag{1.98}$$

and

$$[a_{r^m}^{m\dagger}, a_{s^{m'}}^{m'\dagger}] = 0. \tag{1.99}$$

Following Christiansen, the vibrational Hamiltonian is rewritten in terms of these operator as,

$$H_{vib} = \sum_{t=1}^{N} c_t \prod_{m=1}^{M} h^{m,t}. \tag{1.100}$$

Here,

$$h^{m,t} = \sum_{r^m, s^m} h_{r^m, s^m}^{m,t} a_{r^m}^{m\dagger}, a_{s^m}^m, \tag{1.101}$$

and

$$h_{r^m, s^m}^{m,t} = \langle \phi_{r^m}^m (q_m) | h^{m,t} | \phi_{s^m}^m (q_m) \rangle. \tag{1.102}$$

The vibrational ground state function is parametrized with exponential operator in usual coupled cluster fashion

$$\Psi_{gr} = exp(T) |\Phi_i\rangle, \tag{1.103}$$

with $|\Phi_i\rangle$ a reference Hartree product function. Usually a converged VSCF function is taken as reference function for better convergence. T is the cluster operator that contains one body, two body etc excitation operators.

$$T = T_1 + T_2 + T_3 + \cdots + T_M = \sum_{j=1}^{M} \sum_{\mu_j} t_{\mu_j} \tau_{\mu_j}. \tag{1.104}$$

Here, t_{μ_j} denotes the cluster amplitudes and τ_{μ_j} denotes excitation operator. The expression of these excitation operator is not as straightforward as in electronic structure theory. Here each excitation operator should specify both the excitation level as well as the mode in which the excitation is taking place. Note that each mode has one and only one occupied modal. So, for example, one body operator will annihilate any of these occupied level (i^{m_1}) and create a vibration to the virtual level of the same mode. So, the expression for T_1 is given by

$$T_1 = \sum_{m_1}^{M} \sum_{a^{m_1}} t_{a^{m_1}}^{m_1} a_{a^{m_1}}^{m_1 \dagger} a_{i^{m_1}}^{m_1}. \tag{1.105}$$

Similarly,

$$T_2 = \sum_{m_1 < m_2}^{M} \sum_{a^{m_1}} \sum_{a^{m_2}} t_{a^{m_1}}^{m_1} a_{a^{m_1}}^{m_1 \dagger} a_{i^{m_1}}^{m_1} a_{a^{m_2}}^{m_2 \dagger} a_{i^{m_2}}^{m_2}, \tag{1.106}$$

and so on.

The Schrödinger equation using coupled cluster wave function of Eq. (1.103) becomes,

$$H exp(T)|\Phi_i\rangle = E_{gr} exp(T)|\Phi_i\rangle. \tag{1.107}$$

The working equations for ground state vibrational CC are obtained in usual fashion; i.e. pre-multiplying by $exp(-T)$ and projecting with reference function to get ground state energy and with excited states to get cluster amplitudes,

$$\langle \phi_i | exp(-T) H_{vib} exp(T) | \phi_i \rangle = E_{gr} \tag{1.108}$$

$$\langle \mu | exp(-T) H_{vib} exp(T) | \phi_i \rangle = 0. \tag{1.109}$$

.

The Eq.(1.109) is a set of coupled nonlinear equations and has to be solved iteratively. Once the values of the amplitudes are known, the coupled cluster ground state energy can be obtained from Eq.(1.108).

As stated before, unlike electronic coupled cluster method where double excitation is the most important one for the calculation of correlation energy of the ground state,

43

there is no such natural choice for vibrational coupled cluster method. Christiansen has pointed that there are several ways to approximate the vibrational coupled cluster equations. These different approaches are explained extensively in the reference [75]. For example, One way is to truncate the cluster expansion in Eq. 1.104 and the excitation manifold up to certain maximum excitation level, say n_{max}. T_1 operator will excite one modal from each mode, T_2 will excite from two modes at a time and so on. So, when $n_{max} = M$ the vibrational wave function corresponds to exact ground state functions. Another choice of approximating the VCC is based on the importance of the excitation level defined by the Hamiltonian. For example, if the Hamiltonian contains term operating in mode m_1 and mode m_2, then the single excitations within m_1 and m_2 are included within the first order interaction space, while the excitations including both mode, $m_1 m_2$ are included in the second order space. If the Hamiltonian contains the term $m_1 m_2$ then the first interaction space contains both double excitations $m_1 m_2$ as well as single excitations within m_1 and m_2 modes.

For calculations of excited states energies coupled cluster linear response theory is used so far in basis set representation. The linear response function describing the linear response of the expectation value of X to the perturbation Y at frequency ω_Y is given by

$$\langle\langle X, Y \rangle\rangle_{\omega_Y} = P^{XY} \sum_{k \neq 0} \frac{\langle \Psi_0 | X | \Psi_k \rangle \langle \Psi_k | Y | \Psi_0 \rangle}{\omega_Y - \omega_k}. \tag{1.110}$$

The index k runs over all unperturbed states except the ground state. $\omega_k = E_k - E_0$ is the difference between the energies of the unperturbed excited state and the ground state and P^{XY} is a permutation operator. The linear response function has poles at energies ω_Y corresponding excitation energies of the system.

1.11.2 One dimensional anharmonic oscillator in bosonic representation:

In 80's there were a few studies on one dimensional anharmonic oscillators based on coupled cluster method in bosonic representation [65–67]. Historically, the first application was done using a pure quartic term in the anharmonic potential [65]

44

$$H = \frac{1}{2}p^2 + \frac{1}{2}x^2 + \lambda x^4, \lambda > 0. \tag{1.111}$$

Later on the methodology was extended to an anharmonic oscillator with equally weighted cubic and quartic anharmonic potential terms and to standard symmetric double well oscillator [66]. The Hamiltonian in Eq. 1.111 is expressed in terms of the Harmonic oscillator ladder operators a and $a^\dagger$

$$H = \frac{1}{2} + a^\dagger a + \frac{1}{4}\lambda(a + a^\dagger)^4. \tag{1.112}$$

The expressions for a and $a^\dagger$ are given by,

$$a = 2^{-\frac{1}{2}}(x + ip) \tag{1.113}$$

$$a^\dagger = 2^{-\frac{1}{2}}(x - ip) \tag{1.114}$$

A "generalized coherent function" of the type

$$|\phi\rangle = e^{[\frac{t}{2}a^{\dagger 2}]}|0\rangle \tag{1.115}$$

is variationally optimized with respect to variational parameter t to get optimized ground state energy. Although the HO creation operator $a^\dagger$ can be used for the construction of the rest of the elements of Fock space, however, it is more convenient to use new set of creation and annihilation operators defined via the Bogoliubov transformations of a and $a^\dagger$

$$b = (1 - t^2)^{-\frac{1}{2}}(a - ta^\dagger), \tag{1.116}$$

$$b^\dagger = (1 - t^2)^{-\frac{1}{2}}(a^\dagger - ta). \tag{1.117}$$

The optimized function $|\phi\rangle$ acts as a physical vacuum for the operator b, i.e.

$$b|\phi\rangle = 0. \tag{1.118}$$

With these new set of creation and annihilation operator the expression of Hamiltonian becomes,

$$H = E_0 + [\frac{t}{1 - t^2} + \frac{3\lambda}{2}[\frac{1 + t}{1 - t}]^2](b^2 + b^{\dagger^2})$$
$$+ [\frac{1 + t^2}{1 - t^2} + 3\lambda[\frac{1 + t}{1 - t}]^2]bb^{\dagger} \tag{1.119}$$
$$+ \frac{\lambda}{4}[\frac{1 + t}{1 - t}]^2\{(b + b^{\dagger})^4\}$$

where, the curly bracket represents normal ordering of the operator and

$$E_0 = \frac{1}{2} + \frac{t^2}{1 - t^2} + \frac{3\lambda}{4}[\frac{1 + t}{1 - t}]^2. \tag{1.120}$$

Introducing a new parameter $\omega = \frac{1-t}{1+t}$, this expression is rewritten as,

$$E_0 = \frac{1 + \omega^2}{4\omega} + \frac{3\lambda}{4\omega^2}, \tag{1.121}$$

Applying the variation principle to optimize E_0 one gets,

$$\omega - \omega^3 + 6\lambda = 0. \tag{1.122}$$

The Eq.(1.122) guarantees that the coefficients of b^2 and $b^{\dagger^2}$ are zero which is the condition for b and $b^{\dagger}$ operators corresponds to the normal mode. The Hamiltonian now takes the form,

$$H = E_0 + \omega b^{\dagger}b + \frac{\lambda}{4\omega^2}\{(b + b^{\dagger})^4\}, \tag{1.123}$$

with

$$E_0 = \frac{1 + 3\omega^2}{8\omega}. \tag{1.124}$$

It is found that the Hartree approximation gives the ground state energy with error less than 2% for all values of the coupling strength. Next, the coupled cluster wave function for the ground state is parametrized as

$$|\psi\rangle = e^{\hat{S}}|\phi\rangle, \tag{1.125}$$

where, the expression of the operator $\hat{S}$ is given by

$$S = \sum_{n=1}^{\infty} \hat{S}_n \tag{1.126}$$

and

$$\hat{S}_n = S_n (b^\dagger)^n. \tag{1.127}$$

Note that neither the state $|\phi\rangle$ nor $|\psi\rangle$ is normalized but they follow the relation,

$$\langle\phi|\psi\rangle = \langle\phi|\phi\rangle \tag{1.128}$$

The exact ground state Schrödinger equation,

$$H|\psi\rangle = E_{gr}|\psi\rangle \tag{1.129}$$

is now decomposed in the standard coupled cluster fashion, i.e. by pre-multiplying with $e^{-\hat{S}}$ and then projecting with $\langle\phi|$ and $\langle\phi|b^n$ to get respectively the expression for ground state energy and cluster amplitudes $\{S_n\}$ as,

$$E_{gr} = \langle\phi|e^{-\hat{S}}He^{\hat{S}}|\phi\rangle \tag{1.130}$$

$$\langle\phi|b^n(e^{-\hat{S}}He^{\hat{S}})|\phi\rangle = 0, n = 1, 2, \ldots. \tag{1.131}$$

The Eq. 1.131 is a set of infinite number of coupled nonlinear equations and hence to be truncated for practical implementation. The simplest and most natural truncation scheme is so-called SUB(n) approximation. In this approximation scheme, all S_i with $i > n$ are set to zero and all lower n equations are solved consistently. Once the amplitudes $\{S_n\}$ are determined, the ground state energy is obtained from Eq. 1.130.

Due to nonlinear nature of Eq. 1.131 one gets multiple solutions with any level of truncation or may be with the untruncated series. Kaulfuss and Attenbokum [67] performed a stability analysis on the solutions by introducing temperature dependence and requiring stability against thermal fluctuations to get the desired solution for the ground state. Bishop and co-workers [66] proposed a numerical solution using hybrid Powell method.

Emrich parametrization [187] is used to describe the excited states. Here, the excited states are parametrized with a linear excitation operator operating on CCM ground state wave function

$$\psi' = \hat{S}'e^{-\hat{S}}|\phi\rangle = \hat{S}'|\psi\rangle. \tag{1.132}$$

The excitation correlation operator $\hat{S}'$ is defined in similar way of ground state correlation operator, i.e.

$$\hat{S}' = \sum_{n=1}^{\infty} \hat{S}'_n \qquad (1.133)$$

and,

$$\hat{S}'_n = S'_n(b^{\dagger})^n. \qquad (1.134)$$

With a little algebraic manipulation one can easily get the expression for the working equations for the excited states as,

$$[H, \hat{S}']|\psi\rangle = (E' - E_{gr})\hat{S}'|\psi\rangle. \qquad (1.135)$$

The excitation energies are calculated directly from this equation. The set of coefficients $\{S'_n, n = 1, 2, \dots\}$ is obtained from the equation

$$(n!)^{-1}\langle\phi|b^n(e^{-\hat{S}}[H, \hat{S}']e^{\hat{S}}|\phi\rangle = (E' - E)S'_n, n = 1, 2, \dots. \qquad (1.136)$$

This is a set of linear equations for the unknown set of coefficient S'_n solely depends on the prior knowledge of ground state correlation parameters S_n. Just like the ground state correlation operator, the infinite expansion of S'_n in Eq (1.134) is also truncated up to a finite approximation for practical applicability. The SUB(m,n) truncation scheme means that the S operator of ground state wave function expansion is truncated at 'n' level and all S'_j with $j > m$ are set to zero. The lower m linear equations are solved by diagonalizing the transformed Hamiltonian $e^{-\hat{S}}He^{\hat{S}}$ in the excited manifold defined by the approximation in $\hat{S}'$.

Bishop and co-workers studied the convergence pattern of the coupled cluster state energies with respect to the rank of both ground state cluster operator $\hat{S}$ as well as excited state correlation operator $\hat{S}'$ [66]. It is found that the ground state and lower lying excited states of the anharmonic oscillator are well represented even with low rank of operators. However, for higher excitation operator one should go for higher rank of $\hat{S}'$. The ground state $\hat{S}$ does not have significant role to improve the excited states energies. In other words, the excitation energies are converged with the rank of $\hat{S}$ operator.

One notes that the transformed Hamiltonian is manifestly non-Hermitian. It causes no problem in the exact limit i.e. when $m, n \rightarrow \infty$. However, in the practical implementation of the Emrich formalism, i.e. at finite SUB(m,n) approximation, one may get complex eigenvalues in the excited state spectrum. Bishop and co-workers extensively studied the nature of the complex eigenvalues appear in the spectrum by varying m, n values and the perturbation parameter λ. It is found that at a fixed SUB(m,n) approximation, complex eigenvalues appear beyond certain value of λ. The number of complex pair increases with the increase of λ. This indicates that as anharmonicity increases, the approximation for both ground and excited states becomes inadequate. Again if one increases the value of m keeping n and λ fixed, the complex eigenvalues arise after some point in the higher energy region. Increasing in the value m generates more complex states. This behavior of energy spectrum is quite expected since the Emrich parametrization of the excited states is solely dependent on the correlation of the ground state, the lower lying states are well described but the higher states are not. The failure of the approximation results complex eigenvalues in the higher energy regime.

1.11.3   Bosonic representation for molecular vibrations

The representation described in the previous subsection is implemented to study the nature of anharmonic molecular vibrations. In the bosonic representation for molecular vibrational study [68–71], a multi-dimensional Gaussian of the type

$$\psi_t = exp[\sum_i -\omega_i(Q_i - Q_i^0)] \tag{1.137}$$

is variationally optimized with respect to ω_i and Q_i^0. This optimized Hartree product acts as vacuum for the HO annihilation operator a

$$a|\psi_t\rangle = 0 \tag{1.138}$$

The HO ladder operators are used to construct the rest of the elements of the Fock space. The vibrational Hamiltonian for molecular system in terms of HO ladder operator is

a bosonic Hamiltonian that does not commute with number operator because the HO ladder operators create/annihilate quanta of energy rather than physical particles.

This approach has the advantage of treating overtone and multi-mode combination states of similar energy on equal footing. For example, a third overtone state of mode 1 and a three mode combination state with one quantum of energy in each of the three modes 1, 2, 3 are reached from the vacuum state by a three boson creation operator. In the basis set representation these two excitations are represented by a single particle excitation operator and a three particle excitation operator respectively. Since the interaction terms that couple these two states to the ground state come at the same order of anharmonic potential (cubic term) and for a class of equivalent vibrational modes that have similar zeroth order frequencies, it would be more appropriate to treat these terms on equal footing in the cluster operator. This is possible only in the boson representation. Representing the vibrational wave function by an exponential ansatz in terms of ladder operator has another feature. The resulting functions are parametrized in terms of the complete set of harmonic oscillator eigenfunctions, making the result (to a limited extent) independent of the basis set used.

The first molecular application was reported by Prasad and co-workers [68]. Coupled cluster linear response theory (CCLRT) is used for the description of excited states. These authors truncated the cluster operator at four bosons and showed that the approximation is fairly good. In a later work Prasad [70] showed that expectation values and transition matrix elements could also be obtained reliably at this level of approximation.

1.12   Objective and scope of the thesis

The vibrational coupled cluster study in bosonic representation is still limited. In this thesis, we planned to undertake a systematic study on the convergence pattern of vibrational state energies with respect to the rank of cluster operator at ground state level as well as excitation operator at CCLRT level. The results are compared with the converged full CI

50

results. A systematic comparison between CCM and full CI method is made based on CPU time required in the calculations. As has been seen in the one dimensional anharmonic oscillator study, the CCLRT method generates complex eigenvalues as a result of diagonalization of non-Hermitian transformed Hamiltonian. To eliminate these complex eigenvalues in an approximate manner we apply *extended coupled cluster approach* in the same spirit of Arponen. A convergence study is made on the rank of different type of operators after Arponen type of double similarity transformation in the ECCM approach.

In the third chapter we use the effective operator approach based on CCLRT to calculate the expectation values and transition matrix elements. The convergence studies of these non-energetic properties are done with respect to different level of approximation of excitation operator at CCLRT level. The ECCM method is also used to calculate these properties and its significance over NCCM approach is analyzed extensively.

The coupled cluster linear response theory works extremely well in the lower energy region of vibrational spectra. However it fails to describe the energetically higher states due to linear nature of the excitation operator. In the fourth chapter we formulate the *multi-reference coupled cluster method* in bosonic representation. Unlike electronic structure theory, we used non-normal ordering of the excited state cluster operator. This gives state specific description of the excited states.

In the last chapter, we explore the possibility of the calculation of non-energetic properties within multi-reference coupled cluster framework. We also highlight the possibility of introducing the rotational contribution to the vibrational energy levels in the framework of coupled cluster method in bosonic representation.

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Chapter 2

Vibrational Coupled Cluster Method in bosonic representation: Convergence studies

2.1 Introduction

The coupled cluster method [1–5] has been established as the-state-of-the-art method for describing quantum many body method in general and electronic structures of atoms and molecules in particular. Recently, there have been few attempt to describe molecular anharmonic vibrational spectra by coupled cluster method[6–18]. As mentioned in the first chapter, there are two different representations possible for vibrational coupled cluster formalism. The first one is the basis set representation [6–12] where single mode creation/annihilation operators are used to define excitations and the second approach is the bosonic representation [13–18] where simple harmonic oscillator ladder operators are used as the excitation operators. The bosonic representation of coupled cluster method to describe the molecular vibrational spectra offers some advantages over the basis set representation. As described in the first chapter, different class of vibrational modes have

similar range of frequencies. Consequently, an overtone band and a combination band can have similar energy. The bosonic approach has the advantages of treating overtone and combination states of similar energy on equal footing. Secondly, unlike basis set approach, this approach is invariant under any arbitrary rotation in the coordinate space.

In the bosonic approach the ground state function for coupled cluster method is decomposed in to a variationally optimized Gaussian product function $|\Phi_{ref}\rangle$ (Hartree product) and an exponential wave operator operating on it

$$|\Psi_g\rangle = e^{(S)}|\Phi_{ref}\rangle. \tag{2.1}$$

The cluster operator (S) consists of connected singles, doubles, triples up to n-truple excitation operators. The cluster matrix elements are determined from the equation,

$$\langle\Phi_e|e^{-S}He^S|\Phi_{ref}\rangle, \tag{2.2}$$

where, $|\Phi_e\rangle$ are excited states. The coupled cluster linear response theory [19–22] is used to obtain the excited states. In this method, the excited state energies are obtained as the eigenvalues of the similarity transformed effective Hamiltonian H_{eff},

$$H_{eff} = exp(-S)Hexp(S), \tag{2.3}$$

$$H_{eff}R = RE. \tag{2.4}$$

The effective Hamiltonian matrix is constructed in a suitably truncated basis defined by a linear excitation operator and diagonalized to obtain the transition energies. The vibrational coupled cluster method in bosonic representation was introduced by Prasad and co-workers [17]. These authors truncated the cluster operator at four bosons and showed that the approximation is fairly good. In this chapter we study the convergence pattern of vibrational ground state and excited state energies with respect to the rank of cluster operator. We truncate the cluster operator up to six boson level and study the effect of those truncations on the ground state energy and the excited state spectrum. The

effect of different level of truncations of the excitation operator in the CCLRT level on the energy spectrum is also analyzed.

The effective Hamiltonian defined in Eq. 2.3 is manifestly non-hermitian. This poses no problem in the exact calculation. However, in the practical implementation due to truncation of the S operator at some finite level, the effective Hamiltonian can and does on occasion, develop complex eigenvalues in the energy spectra [23]. One way of eliminating such complex eigenvalues is to use a unitary transformation. Such an approach, as we have seen in the first chapter, leads to infinite order polynomial equations for the cluster matrix elements even when it is truncated at some level, introducing uncontrolled approximations. An in between way out is to carry out a second similarity transformation in the spirit of extended coupled cluster method (ECCM) formulated by Arponen [24]. In this study we applied this approach to eliminate the complex eigenvalues. As discussed in the first chapter, the second similarity transformation is generated using a de-excitation operator σ,

$$H_{eff} = e^{\sigma} e^{-S} H e^{S} e^{-\sigma}. \tag{2.5}$$

The effect of double similarity transformation on the energy spectrum is also analyzed with respect to the truncation in the σ operator.

This chapter is organized as follows. First we give a brief description of vibrational coupled cluster method in bosonic representation followed by description of ECCM based approach. Next, we present some results of the implementation of vibrational coupled cluster theory. Finally some concluding remarks are given.

2.2 The vibrational coupled cluster method in bosonic representation:

At the outset, the formulation of vibrational coupled cluster method assumes the Watson Hamiltonian [25] in normal coordinates described in the first chapter. Within the Born-Oppenheimer approximation, the expression of Watson Hamiltonian for non-rotating

molecules is given by,

$$H = \frac{1}{2} \sum_k P_k^2 + V(Q) + V_c + V_W. \qquad (2.6)$$

Here, Q_i and P_i represent the mass weighted normal coordinates and their conjugate momenta. $V(Q)$ is the potential energy function. This is often approximated by a quartic potential in the Taylor series expansion,

$$V = \frac{1}{2} \sum_i \omega_i^2 Q_i^2 + \sum_{i \leq j \leq k} f_{ijk} Q_i Q_j Q_k + \sum_{i \leq j \leq k \leq l} f_{ijkl} Q_i Q_j Q_k Q_l. \qquad (2.7)$$

V_c and V_W are the Coriolis coupling and the Watson's mass term respectively.

The coupled cluster approach to molecular anharmonic vibration consists of three steps. In the first step, as mentioned in introduction, we need a vacuum state to construct the Fock space. We used Hartree approximation to construct the vacuum state. A multi-dimensional Gaussian ansatz

$$\psi = N exp\big[(\sum_i \omega_i (Q_i - Q_i^0)^2 / 2)\big], \qquad (2.8)$$

is optimized with respect to variational parameters ω_i and Q_i^0 and to get the vacuum state. Since the Coriolis coupling is relatively week we have ignored it in the Hartree approximation. The equations for the variational parameters ω_i and Q_i^0 are [17],

$$2 f_{ii} Q_i^0 + \sum_{j \leq k} f_{ijk} Q_j^0 Q_k^0 + \sum_{j \leq k \leq l} f_{ijkl} Q_j^0 Q_k^0 Q_l^0 + \sum_j \frac{f_{ijj}}{2\omega_j} + \sum_{jl} \frac{f_{ijjl} Q_l^0}{2\omega_j} = 0, \qquad (2.9)$$

$$\omega_i^0 = 2(f_{ii} + \sum_j f_{iij} Q_j^0 + \sum_j \frac{f_{iijj}}{2\omega_j} + \sum_{j \leq k} f_{iijk} Q_j^0 Q_k^0). \qquad (2.10)$$

The Hartree product is not essential for the formulation of coupled cluster method. However, it is found that it improves the convergence of CCM equations especially for excited states.

Now, we define the harmonic oscillator ladder operator in usual fashion,

$$a_i = \sqrt{\frac{\omega_i}{2}} (Q_i - Q_i^0 + \frac{1}{\omega_i} \frac{d}{d(Q_i - Q_i^0)}) \qquad (2.11)$$

$$a_i^\dagger = \sqrt{\frac{\omega_i}{2}} (Q_i - Q_i^0 - \frac{1}{\omega_i} \frac{d}{d(Q_i - Q_i^0)}). \qquad (2.12)$$

74

The optimized Hartree state is the vacuum state $|0\rangle$ for the operator a_i

$$a_i|0\rangle = 0. \tag{2.13}$$

The ground state wave function is now parametrized as,

$$\Psi_g = e^S|0\rangle. \tag{2.14}$$

The cluster operator is given by

$$S = \sum_{n=1}^{\infty} S_n, \tag{2.15}$$

where, S_n consists of n quanta excitation operators. Since the wave operator operates on the physical vacuum, the excitation operators contain only creation operators ($a^\dagger$). Generally a k-body excitation operator S_k has k creation operators and contains $\Theta(N^k)$ terms in it. Here, N is the number of vibrational modes in the molecule. For example, S_3 is given by

$$S_3 = \sum_{i \leq j \leq k} S_{ijk} a_i^\dagger a_j^\dagger a_k^\dagger. \tag{2.16}$$

The number of such three quantum excitation operators is $N(N+1)(5N+1)/6$, in the absence of any symmetry.

The working equations for the cluster elements and ground state energy are given by

$$\langle e|H_{eff}^N|0\rangle = 0, \tag{2.17}$$

$$E_{gs} = \langle 0|H_{eff}^N|0\rangle. \tag{2.18}$$

Here,

$$H_{eff}^N = e^{-S}He^S. \tag{2.19}$$

The effective Hamiltonian H_{eff}^N may be evaluated either by Hausdorff multi-commutator expansion or by usual diagrammatic techniques. We note here that the Hamiltonian in Eq. 2.19 includes the Coriolis interaction also.

The solution of Eq. 2.18 gives the coefficients of the cluster operators. Since the potential energy function in the Hamiltonian is approximated at quartic level, the equations terminate after the fourth commutator in the Hausdorff expansion. These equations

are coupled nonlinear equations and have to be solved iteratively. They can be written compactly as

$$A + BS + CS^2 + DS^3 + ES^4 = 0. \tag{2.20}$$

With a little algebraic manipulation, the Eq. 2.20 can be written as,

$$S = B_0^{-1}[A + (B - B_0)S + CS^2 + DS^3 + ES^4]. \tag{2.21}$$

Starting from a guess S-vector, the equations are iterated until the input and output S-vectors are within a preset threshold. Since the Hartree approximation is close to exact ground state, the cluster elements are generally small. Once the cluster matrix elements are obtained, the ground state energy is calculated from Eq. 2.18.

In the last step, excited state energies are obtained from the CCLRT. In this method, the excited states are parametrized as

$$|\Psi_{ex}\rangle = e^S \Omega |0\rangle. \tag{2.22}$$

Here, Ω is a linear excitation operator contains only the creation operators,

$$\Omega = \sum_i \Omega_i a_i^\dagger + \sum_{i \leq j} \Omega_{ij} a_i^\dagger a_i^\dagger + \dots. \tag{2.23}$$

The transition energies ΔE and the matrix elements of Ω are obtained from,

$$[H_{eff}^N, \Omega]|0\rangle = \Delta E \Omega |0\rangle. \tag{2.24}$$

Solving this equation is equivalent to diagonalization of H_{eff}^N in the exited state manifold defined by the approximation in Ω.

2.2.1 ECCM based approach:

As mentioned earlier, an approximate H_{eff}^N can lead to complex eigenvalues for the excited state energies due to the loss of hermiticity in the effective Hamiltonian. We apply ECCM approach to eliminate the complex eigenvalues of the effective Hamiltonian in

approximate manner. In this approach the effective Hamiltonian is generated using a second similarity transformation,

$$H_{eff}^E = e^\sigma e^{-S} H e^S e^{-\sigma} = e^\sigma H_{eff}^N e^{-\sigma}. \tag{2.25}$$

Here, σ is composed of only de-excitation operators,

$$\sigma = \sum_i \sigma_i a_i + \sum_{i \leq j} \sigma_{ij} a_i a_j + \ldots. \tag{2.26}$$

The matrix elements for σ are obtained from

$$\langle 0 | H_{eff}^E | e \rangle = 0. \tag{2.27}$$

The matrix elements of H_{eff}^N between the vacuum state and the excited states are zero due to Eq. 2.18. This must be taken in to account while constructing H_{eff}^N in Eq. 2.25.

While the original ECCM formulation by Arponen requires a variational solution to the cluster matrix elements, we prefer a method of moment approach based on Eq. 2.27 in the spirit of conventional CCM. According to Lie algebraic theorem, the equations for the S matrix elements are decoupled from the σ matrix elements in the exact limit [23]. We assume that this holds even in approximate calculations. The Eq. 2.18 and Eq. 2.27 are solved sequentially to obtain the S and σ matrix elements.

The ECCM approach eliminates the loss of hermiticity up to second order, because the matrix elements S and σ are identical up to first order in the perturbation V. The second similarity transformation does not affect the ground state energy. However, since the effective Hamiltonian matrix elements change, the transition energies change.

2.3 Results and Discussion

The formulation developed in previous sections are applied to few tri-atomic and tetra atomic molecules. Our primary goal in these calculations is to analyze the convergence properties of the cluster operator and its effects on the ground and excited state energies. The cluster operators S and σ and the excitation operator Ω were truncated at different levels up to a maximum of six bosons. The results are presented below.

2.3.1 Formaldehyde:

Recently, there have been several studies on the vibrational spectrum of formaldehyde using different *ab initio* methods [26–31]. Accordingly, we have applied our method to study the vibrational spectrum of this molecule at different level of approximations. Although, there are many force fields of formaldehyde available in the literature, we have taken the force field and the Coriolis coupling data from Romanowski et. al [26] and compared our results with the full CI results presented there.

We have studied the convergence pattern of vibrational excited state energies with the rank of both the cluster operator S and excitation operators Ω of NCCM and CCLRT method respectively. The variations of the energy levels with different approximations to the cluster operator are presented in table 2.1. In all these calculations Ω was expanded up to six boson level. As can be seen, the state energies have converged within $1cm^{-1}$ respect to cluster operator by about S_4. In table 2.2, we present the convergence pattern of the vibrational levels by varying the truncation level of Ω keeping cluster operator S fixed at six boson level. In about half of the states, the state energies have converged by Ω_6. While for the remaining states the state energies are not converged even at this level. This indicates that a relatively higher order approximation is warranted for the linear excitation operator.

The best agreements with CI results were found for the fundamental excited states. Except 5_1 state all other fundamental states energies are within $1cm^{-1}$ with respect to full CI results with four boson operator in both cluster operator S and excitation operator Ω. Although in most of the cases, the energies of the overtones as well as the combinations levels are found to be converging with increase of excitation operator, for some states, especially when the fifth mode is involved, we got large deviations.

The results with different level of truncation of Ω operator have been compared after double similarity transformation in table 2.3. The results are also compared with full CI

Table 2.1: Variation of vibrational energies of formaldehyde with varying the cluster operators S from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI^a
000 000	A_1	5777.20	5777.14	5777.17	5777.2
001 000	A_1	7278.03	7277.97	7278.00	7277.5
010 000	A_1	7524.57	7524.51	7524.54	7524.5
000 200	A_1	8093.26	8093.23	8093.28	8092.3
000 002	A_1	8265.46	8265.40	8265.43	8266.4
100 000	A_1	8558.87	8558.66	8558.77	8558.8
002 000	A_1	8776.15	8776.08	8776.11	8774.8
011 000	A_1	9017.87	9017.81	9017.84	9017.3
020 000	A_1	9256.41	9256.35	9256.38	9256.2
000 011	A_1	9854.99	9854.87	9854.94	9864.1
101 000	A_1	10024.47	10024.24	10024.34	10048.2
110 000	A_1	10305.40	10305.18	10305.29	10306.7
200 000	A_1	11279.59	11278.90	11279.13	11274.9
000 020	A_1	11420.31	11419.87	11420.00	11476.6
000 101	A_2	8190.54	8190.52	8190.56	8193.0
000 110	A_2	9754.88	9754.73	9754.81	9777.5
000 100	B_1	6937.75	6937.71	6937.75	6937.8
001 100	B_1	8432.93	8432.89	8432.92	8432.6
010 100	B_1	8676.43	8676.38	8676.41	8676.5
100 100	B_1	9692.85	9692.73	9692.85	9692.0
000 001	B_2	7023.16	7023.11	7023.14	7022.9
001 001	B_2	8497.52	8497.38	8497.43	8478.3
000 010	B_2	8620.72	8620.52	8620.61	8635.0
010 001	B_2	8773.06	8773.01	8773.04	8780.5
100 001	B_2	9780.73	9780.53	9780.64	9783.7
001 010	B_2	10104.19	10104.01	10104.09	10128.9
010 010	B_2	10351.57	10351.36	10351.44	10362.2
100 010	B_2	11306.34	11305.70	11305.90	11366.8

[a]See [26].
The excitation operator in these cases is truncated at six boson.
All results are in cm^{-1} units.

Table 2.2: Variation of vibrational energies of formaldehyde with varying the excitation operators Ω from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI^a
000 000	A_1	5777.20	5777.14	5777.17	5777.2
001 000	A_1	7278.07	7278.01	7278.00	7277.5
010 000	A_1	7524.56	7524.54	7524.54	7524.5
000 200	A_1	8094.94	8093.32	8093.28	8092.3
000 002	A_1	8267.04	8265.56	8265.43	8266.4
100 000	A_1	8559.13	8558.83	8558.77	8558.8
002 000	A_1	8777.97	8776.30	8776.11	8774.8
011 000	A_1	9019.20	9017.96	9017.84	9017.3
020 000	A_1	9257.46	9256.42	9256.38	9256.2
000 011	A_1	9860.61	9856.66	9854.94	9864.1
101 000	A_1	10026.96	10024.99	10024.34	10048.2
110 000	A_1	10305.15	10305.55	10305.29	10306.7
200 000	A_1	11286.73	11280.45	11279.13	11274.9
000 020	A_1	11431.31	11423.71	11420.00	11476.6
000 101	A_2	8192.41	8190.65	8190.56	8193.0
000 110	A_2	9760.81	9756.35	9754.81	9777.5
000 100	B_1	6937.78	6937.75	6937.75	6937.8
001 100	B_1	8435.07	8433.09	8432.92	8432.6
010 100	B_1	8678.11	8676.53	8676.41	8676.5
100 100	B_1	9696.86	9693.90	9692.85	9692.0
000 001	B_2	7023.19	7023.14	7023.14	7022.9
001 001	B_2	8498.70	8497.57	8497.43	8478.3
000 010	B_2	8621.41	8620.71	8620.61	8635.0
010 001	B_2	8774.46	8773.16	8773.04	8780.5
100 001	B_2	9784.08	9781.62	9780.64	9783.7
001 010	B_2	10110.30	10105.85	10104.09	10128.9
010 010	B_2	10353.98	10352.36	10351.44	10362.2
100 010	B_2	11317.75	11308.73	11305.90	11366.8

^{a}See [26].
The cluster operator S in these cases is truncated at six boson.
All results are in cm^{-1} unit.

Table 2.3: Variation of vibrational energies of formaldehyde after Arponen type of double similarity transformation with varying the excitation operators Ω from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI^a
000 000	A_1	5777.20	5777.14	5777.17	5777.2
001 000	A_1	7278.85	7278.85	7278.85	7277.5
010 000	A_1	7524.72	7524.72	7524.72	7524.5
000 200	A_1	8095.42	8096.35	8096.35	8092.3
000 002	A_1	8267.44	8267.34	8268.33	8266.4
100 000	A_1	8557.40	8557.33	8557.87	8558.8
002 000	A_1	8777.98	8777.88	8777.87	8774.8
011 000	A_1	9019.12	9019.04	9019.03	9017.3
020 000	A_1	9256.81	9256.75	9256.74	9256.2
000 011	A_1	9860.62	9856.42	9856.19	9864.1
101 000	A_1	10026.88	10025.49	10025.37	10048.2
110 000	A_1	10304.94	10304.10	10304.01	10306.7
200 000	A_1	11281.05	11276.32	11275.22	11274.9
000 020	A_1	11429.75	11421.12	11418.82	11476.6
000 101	A_2	8192.64	8192.55	8193.55	8193.0
000 110	A_2	9760.61	9756.77	9754.62	9777.5
000 100	B_1	6938.94	6938.94	6938.94	6937.8
001 100	B_1	8435.21	8435.10	8435.09	8432.6
010 100	B_1	8678.15	8678.05	8678.04	8676.5
100 100	B_1	9697.15	9695.32	9695.23	9692.0
000 001	B_2	7024.06	7024.06	7024.06	7022.9
001 001	B_2	8499.48	8499.36	8499.35	8478.3
000 010	B_2	8619.84	8619.74	8619.73	8635.0
010 001	B_2	8773.91	8773.82	8773.81	8780.5
100 001	B_2	9784.28	9782.53	9782.41	9783.7
001 010	B_2	10110.26	10106.25	10105.99	10128.9
010 010	B_2	10353.84	10351.49	10351.35	10362.2
100 010	B_2	11317.37	11301.86	11300.11	11366.8

[a]See [26].

The cluster operator S in these cases is truncated at six boson.

All results are in cm^{-1} unit.

Table 2.4: Comparison between the basis set approach and the bosonic approach.

States	VCC(2)	VCC(3)	VCC(4)	VCC(5)	Our results[a]
100 000	1.0118	0.3518	0.0106	0.0001	-0.10
010 000	1.0262	0.1275	0.0072	0.0001	0.00
001 000	2.2399	0.3806	0.0109	0.0001	-0.50
000 100	1.3572	0.0123	0.0159	0.0003	-0.10
000 001	5.2697	1.4940	0.0114	0.0000	-14.39
000 010	2.7320	0.4775	0.0045	0.0000	0.20
200 000	11.6249	4.4018	1.3348	0.0835	4.23
020 000	4.6568	0.4866	0.0282	0.0007	0.20
002 000	8.1959	1.8346	0.0763	0.0010	1.80
000 200	3.2624	0.3050	0.0492	0.0014	1.00
000 020	-4.1974	31.6393	0.5399	0.0046	56.4
000 002	10.4645	2.2359	0.0273	0.0002	-1.00

[a]The results are with six boson rank of the excitation operator.
The error with respect to full CI are presented here. The Basis set approach results are taken from reference [10]

results. We found that, the improvement of the results due to double similarity transformation over the NCCM is marginal. However, the purpose of doing similarity transformation was to recover the complex eigenvalues. We have found that some of states e.g. 1_3 have complex eigenvalues in the NCCM based calculation. After the double similarity transformation the state energy becomes real.

As mentioned earlier, there are large errors in CCM calculation in the excited states where the fifth mode is excited. The deviation exists even in the case of the fundamental 5_1. We have compared our results with the results obtained by Seidler and Christiansen [10] using coupled cluster response theory in basis set approach. In table 2.4, we present the relative errors found in these two different approaches with respect to full CI. It is found that even in basis set approach, VCC3 approximation gives similar errors, e.g. $31.64 cm^{-1}$ in 5_2 state. The improvements of results were found in VCC4 and VCC5 approximations. Since these states have large contributions from higher quanta excitations (e.g. the 5_2 state has 0.31 weights from $3_1 5_1 6_1$), they can not be described by low level excitations [10]. Four body and five body terms in VCC4 and VCC5 provide such higher

excitations to describe these states correctly. Because we truncate the excitation operator based on the number of quanta it generates, it misses out several states that are energetically closed to those that are already included in it due to large mismatch between the stretching and bending mode. The absence of these states affects the movement of the zeroth order states significantly. For example the 5_2 state is energetically close to 4_5 and $2_3 6_1$ states. The later states are represented by four and five boson operators in Ω. However, there are very few terms in Ω that generate states which can push these states down. Because of this, the high energy states are pushed up and down unevenly. This does not affect the fundamental states significantly because to describe the fundamentals we have sufficient numbers of excited levels in six quanta level of excitations.

2.3.2 Water

The water molecule has long been a benchmark molecule for the study of *ab inito* vibrational spectra [32–36]. It is a highly anharmonic molecule due to its low barrier of inversion. In addition, it is an archetypical local mode molecule due to large disparity between masses of oxygen and hydrogen. Consequently a description of its energy spectrum is a good test for any theoretical method based on normal mode representation. There have been extensive studies on the potential energy surface of water molecule in the literature using very accurate methods of electronic structure. We have taken the PES from the work of Császár *et al* [35]. This PES is highly accurate calculated by using CCSD(T) method with aug-cc-pVQZ basis set. The Coriolis coupling terms were not included in this potential energy data. We have compared the CCM results with full CI results calculated by us. We present CCM results of all states with three quanta excitations and some of the relatively lower lying four quantum excited states. For full CI we have used 8-16-8 harmonic oscillator basis set and have verified that these numbers are converged with respect to basis set.

The energies of the excited states for different levels of truncations in S are given in table 2.5. In all these calculations the excitation operator was truncated at Ω_6 level.

Like formaldehyde, here also the state energies are converged with as low as four boson operator in S. For the lower lying states e.g for the fundamentals and two quanta excited states the energies reached the converged full CI values. However, for higher excited states the results are still away from full CI. The convergence trends of results in table 2.5 also support the speculation that errors in the state energies of the higher states are due to inadequacy of the excitation operator.

The convergence trends of the state energies with respect to the rank of the excitation operator Ω are presented in table 2.6. The CCM description is excellent for the fundamentals i.e. 1_1, 2_1 and 3_1. The maximum deviation in these cases is only $1.2 \ cm^{-1}$ for 3_1 state. The CCM gives a fairly good description for the overtones states 1_2, 2_2 and 3_2 and the combination states where only two quanta are excited, i.e. $1_1 2_1$, $1_1 3_1$ and $2_1 3_1$. The maximum deviation in these cases is $4.4 \ cm^{-1}$ (for 3_2 state) with six bosons at both the NCCM and CCLRT levels.

The higher energy three quanta and four quanta excited states are not well described at six boson approximation of the excitation operator. In some cases the relative errors between the converged full CI and NCCM method is quite large. It can be seen that these states are not converged with respect to Ω at the six boson level. We find dramatic improvements in these states on increasing the rank of excitation operator from four boson to five boson to six boson rank of the excitation operator. For example, the energy of 2_3 state changes from $9307.92 \ cm^{-1}$ to $9276.88 \ cm^{-1}$ from four boson to six boson rank of the excitation operator. The converged CI energy of this state is $9265.47 \ cm^{-1}$. Since for higher states we need larger effective Hamiltonian matrix, these states are not properly described by six boson approximation in the excitation operator.

In table 2.7 we present the comparisons between the state energies obtained from converged full CI and ECCM results with four, five and six bosons excitation operators. Like the case of formaldehyde, here also the improvement in energies due to double similarity transformation in ECCM is marginal.

Table 2.5: Variation of vibrational energies of water with varying the cluster operators S from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI results
000	A_1	4660.80	4660.75	4660.78	4660.91
010	A_1	6233.51	6233.43	6233.47	6233.56
020	A_1	7776.29	7776.11	7776.13	7774.57
100	A_1	8366.27	8366.11	8366.21	8366.80
030	A_1	9277.33	9276.91	9276.88	9265.47
110	A_1	9894.53	9894.40	9894.52	9894.28
040	A_1	10731.63	10730.95	10730.92	10655.35
120	A_1	11408.67	11408.61	11408.78	11403.33
200	A_1	12043.82	12043.40	12043.62	12042.01
002	A_1	12212.98	12212.55	12212.72	12208.33
130	A_1	12924.39	12924.42	12924.52	12885.89
210	A_1	13511.63	13511.30	13511.51	13491.68
012	A_1	13664.45	13664.01	13664.17	13624.47
220	A_1	15161.33	15161.00	15161.11	14909.26
022	A_1	15405.97	15405.36	15405.49	15044.02
300	A_1	15707.04	15705.98	15706.19	15729.50
102	A_1	16064.46	16064.19	16064.39	15883.60
310	A_1	17190.66	17190.04	17190.17	17097.84
112	A_1	17493.25	17492.42	17492.47	17192.20
001	B_1	8448.54	8448.38	8448.48	8449.69
011	B_1	9949.15	9948.94	9949.06	9948.84
021	B_1	11436.34	11436.06	11436.18	11424.67
101	B_1	12105.98	12105.79	12106.01	12110.22
031	B_1	12911.27	12910.75	12910.78	12866.91
111	B_1	13530.73	13530.40	13530.59	13526.79
121	B_1	14985.74	14985.33	14985.42	14914.91
201	B_1	15734.13	15733.93	15734.07	15803.25
003	B_1	15965.42	15964.37	15964.70	15949.27
211	B_1	17083.12	17082.56	17082.55	17125.70
013	B_1	17311.74	17310.57	17310.65	17252.42

The excitation operator in these cases is truncated at six boson.
All results are in cm^{-1} unit.

Table 2.6: Variation of vibrational energies of water with varying the excitation operator Ω from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI results
000	A_1	4660.80	4660.75	4660.78	4660.91
010	A_1	6233.56	6233.47	6233.47	6233.56
020	A_1	7779.94	7776.66	7776.13	7774.57
100	A_1	8366.21	8366.25	8366.21	8366.80
030	A_1	9307.92	9288.40	9276.88	9265.47
110	A_1	9896.61	9895.02	9894.52	9894.28
040	A_1	10954.31	10789.58	10730.92	10655.35
120	A_1	11423.30	11417.42	11408.78	11403.33
200	A_1	12039.43	12041.30	12043.62	12042.01
002	A_1	12210.46	12211.86	12212.72	12208.33
130	A_1	12931.11	12937.96	12924.52	12885.89
210	A_1	13530.06	13515.64	13511.51	13491.68
012	A_1	13672.83	13665.29	13664.17	13624.47
220	A_1	15252.29	15151.29	15161.11	14909.26
022	A_1	15551.34	15410.31	15405.49	15044.02
300	A_1	15763.84	15713.95	15706.19	15729.50
102	A_1	16193.99	16089.85	16064.39	15883.60
310	A_1	17660.42	17157.39	17190.17	17097.84
112	A_1	18361.71	17630.27	17492.47	17192.20
001	B_1	8448.47	8448.51	8448.48	8449.69
011	B_1	9951.22	9949.19	9949.06	9948.84
021	B_1	11454.03	11442.44	11436.18	11424.67
101	B_1	12102.97	12103.96	12106.01	12110.22
031	B_1	12959.79	12934.88	12910.78	12866.91
111	B_1	13577.31	13538.37	13530.59	13526.79
121	B_1	15313.33	15019.90	14985.42	14914.91
201	B_1	15872.82	15744.71	15734.07	15803.25
003	B_1	15998.52	15964.48	15964.70	15949.27
211	B_1	18360.87	17280.53	17082.55	17125.70
013	B_1	17719.39	17346.89	17310.65	17252.42

The cluster operator in these cases is truncated at six boson.
All results are in cm^{-1} unit.

Table 2.7: Variation of vibrational energies of water after Arponen type double similarity with varying the excitation operator Ω from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI results
000	A_1	4660.91	4660.91	4660.91	4660.91
010	A_1	6234.04	6234.04	6234.04	6233.56
020	A_1	7777.97	7777.55	7777.48	7774.57
100	A_1	8365.18	8365.14	8365.14	8366.80
030	A_1	9303.48	9284.60	9281.30	9265.47
110	A_1	9896.74	9895.80	9895.74	9894.28
040	A_1	10947.99	10781.78	10719.21	10655.35
120	A_1	11421.80	11416.71	11413.74	11403.33
200	A_1	12040.11	12038.37	12037.87	12042.01
002	A_1	12211.90	12210.81	12210.45	12208.33
130	A_1	12924.67	12934.12	12922.66	12885.89
210	A_1	13531.42	13512.37	13509.71	13491.68
012	A_1	13672.55	13662.82	13661.72	13624.47
220	A_1	15250.98	15151.38	15154.88	14909.26
022	A_1	15551.72	15406.90	15400.26	15044.02
300	A_1	15774.90	15705.15	15700.57	15729.50
102	A_1	16210.96	16075.89	16067.61	15883.60
310	A_1	17662.74	17159.70	17185.61	17097.84
112	A_1	18366.82	17641.21	17467.13	17192.20
001	B_1	8447.48	8447.43	8447.43	8449.69
011	B_1	9950.28	9949.89	9949.82	9948.84
021	B_1	11450.92	11439.33	11439.00	11424.67
101	B_1	12102.75	12100.46	12099.72	12110.22
031	B_1	12954.41	12928.99	12904.99	12866.91
111	B_1	13580.11	13534.26	13530.18	13526.79
121	B_1	15312.23	15020.57	14978.72	14914.91
201	B_1	15885.64	15738.81	15727.71	15803.25
003	B_1	16014.10	15968.91	15963.80	15949.27
211	B_1	18365.32	17288.67	17067.91	17125.70
013	B_1	17721.51	17352.46	17306.87	17252.42

The cluster operator in these cases is truncated at six boson.
The energies are in cm^{-1} unit.

2.3.3 Oxygen difluoride

Our third test case is the oxygen difluoride molecule (F_2O). The anharmonic vibrational spectra and the quartic PES of this molecule is calculated by several authors [37–39]. We have taken the quartic force field data from the work of Breidung *et al* [39]. These authors made extensive calculations on the quartic PES using both MP2 method and CCSD(T) method and cc-pVTZ and cc-pVQZ basis set. We choose the PES based on CCSD(T) calculation using cc-pVQZ basis set to apply our methodology. The PES does not include Coriolis coupling terms. In table 2.8, we present the comparisons of state energies with different levels of truncations in excitation operator Ω in CCLRT and converged full CI. The cluster operator is fixed at S_6 level in all these calculations. We compare our results with converged full CI values. 8-16-8 harmonic oscillator basis functions are used for the CI calculation.

The NCCM provides excellent account of the vibrational energy spectrum of oxygen di-fluoride molecule for lower energy states. This molecule is less anharmonic compared to water molecule due to less mass disparity between fluorine and oxygen as compared to that between hydrogen and oxygen in water molecule. Consequently, for this molecule the CCM provides a better description for state energies than water. For the fundamentals and two quanta excited states, the state energies are converged with as low as four boson rank of the excitation operator and they reached the converged full CI values. The maximum error with respect to full CI in these cases is less than $1\ cm^{-1}$. Except $1_1 3_2$ state, all other three quanta excited states are described fairly well with six boson rank in cluster operator in NCCM as well as excitation operator in CCLRT. In case of $1_1 3_2$ state we find large deviation between full CI result and CCM result ($35\ cm^{-1}$) with six boson excitation operator in both NCCM and CCLRT. Even some of the lower lying four quanta excited states e.g. $1_1 2_3$, $1_2 2_2$, $2_3 3_1$ are also reasonably well represented by Ω_6. The other higher energy four quanta excited states are quite away from the converged full CI. These states are not converged with the Ω_6 excitation operator. We find dramatic

Table 2.8: Variation of vibrational energies of oxygen di-fluoride with varying the excitation operators Ω from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI results
000	A_1	1140.57	1140.57	1140.57	1140.58
010	A_1	1605.81	1605.81	1605.81	1605.81
020	A_1	2066.54	2066.48	2066.48	2066.43
100	A_1	2077.69	2077.67	2077.67	2077.71
030	A_1	2525.89	2525.48	2525.31	2525.13
110	A_1	2542.59	2542.24	2542.15	2542.21
002	A_1	2826.67	2826.28	2826.27	2825.35
120	A_1	2989.98	2983.16	2982.17	2981.34
200	A_1	3004.92	2999.23	2998.64	2998.25
012	A_1	3280.97	3279.29	3278.06	3271.08
130	A_1	3503.49	3444.19	3436.37	3435.56
210	A_1	3458.39	3468.31	3459.64	3455.56
102	A_1	3780.61	3770.81	3767.44	3732.10
220	A_1	3976.79	3927.03	3902.54	3908.86
300	A_1	3921.92	3910.53	3918.51	3921.86
112	A_1	4338.04	4235.84	4223.26	4176.64
310	A_1	4477.68	4378.49	4362.45	4379.12
004	A_1	4629.56	4447.42	4423.14	4484.07
202	A_1	4864.29	4673.07	4652.39	4636.15
400	A_1	5014.24	4844.99	4825.46	4845.55
001	B_1	1986.84	1986.85	1986.85	1986.88
011	B_1	2442.80	2442.46	2442.45	2442.40
021	B_1	2896.55	2894.77	2894.18	2893.62
101	B_1	2908.89	2908.18	2908.11	2907.86
031	A_1	3407.09	3345.71	3340.06	3342.43
111	B_1	3361.53	3363.30	3360.89	3362.46
003	B_1	3665.24	3661.68	3659.54	3657.03
121	A_1	3899.21	3825.93	3794.20	3788.95
201	B_1	3830.88	3812.68	3823.86	3823.40
013	A_1	4203.50	4115.33	4109.29	4092.94
103	A_1	4799.79	4661.39	4637.68	4552.11
301	A_1	5003.17	4722.23	4670.35	4734.22

The cluster operator S in these cases is truncated at six boson.
All results are in cm^{-1} unit.

improvements of these energies on increasing the rank of the excitation operator from four boson to five boson to six boson level. These results suggest that one need a higher order truncation in Ω to describe higher energy states accurately.

2.3.4 Hydrogen Sulphide

The hydrogen sulphide (H_2S) is another benchmark tri-atomic molecule for *ab initio* vibrational spectra calculations. Like H_2O, it is a typical local mode molecule due to large mass disparity between the central and the terminal atoms. The two near degenerate stretching modes are strongly coupled. Moreover due to low inversion barrier, the bending mode is quite anharmonic. Thus it provides a good testing ground to apply the CCM method to study its vibrational spectrum.

For PES calculation we have used the GAUSSIAN 03 package [40]. This package generates quartic force field in normal coordinate using Barone's algorithm [41]. The density functional theory (DFT) based method, Becke three-parameter hybrid (B3) functional along with Lee-Yang-Parr (LYP) [43] and aug-cc-pVQZ basis set are used to generate the anharmonic force field values. Geometry optimization is carried out tightly and the ultrafine keyword is used in the DFT calculation as recommended by Barone [42].

In table 2.9 we present the vibrational state energies at different levels of truncation in the excitation operator Ω. The ground state cluster operator is kept fixed at six boson level following the observation that the state energies are saturated with the rank of the ground state cluster operator S at six boson level. We compared our results with the full CI values using 8-16-8 harmonic oscillator basis set. We find that for the ground state and for the fundamentals, the NCCM results are in agreement with the converged full CI results and the values are converged with four boson excitation operator. For all the two quanta excited states, three quanta excited states 2_3, 1_12_2, 1_22_1, $1_12_13_1$ and 3_3 and even four quanta excited state 2_4, the NCCM results are converged with six boson excitation operator and they are very close to the full CI results. The maximum deviation in these cases is only about $4.0\ cm^{-1}$ for 1_22_1 and 1_2 states. In the case of 1_12_3, 2_23_1 and 2_13_3

Table 2.9: Variation of vibrational energies of H_2S with varying the excitation operator Ω from four boson to six boson.

States	Symmetry	Four boson	Five boson	Six boson	CI results
000	A_1	3258.31	3258.31	3258.31	3258.36
010	A_1	4430.84	4430.83	4430.83	4430.88
020	A_1	5596.17	5595.36	5595.34	5595.25
100	A_1	5851.51	5851.54	5851.54	5851.81
030	A_1	6754.80	6751.98	6750.75	6750.20
110	A_1	6997.74	6996.64	6996.48	6996.57
040	A_1	7917.29	7898.93	7893.43	7894.24
120	A_1	8141.89	8139.96	8136.00	8135.72
200	A_1	8411.32	8410.15	8411.42	8407.27
002	A_1	8451.17	8451.64	8451.61	8452.15
130	A_1	9289.89	9278.09	9274.47	9268.51
012	A_1	9524.86	9516.33	9512.05	9497.63
210	A_1	9562.06	9557.46	9556.67	9552.61
022	A_1	10926.89	10799.54	10791.43	10572.59
220	A_1	10803.93	10741.68	10748.57	10653.86
102	A_1	11173.07	11115.50	11098.09	10960.55
300	A_1	11017.39	10987.06	10978.77	11001.70
112	A_1	12751.32	12239.18	12184.94	11998.49
310	B_1	12409.29	12089.54	12005.29	12068.50
001	B_1	5857.85	5857.88	5857.87	5858.48
011	B_1	6988.82	6987.60	6987.57	6987.79
021	B_1	8120.78	8115.72	8112.69	8109.24
101	B_1	8407.07	8406.12	8406.90	8408.56
031	B_1	9268.52	9245.32	9236.09	9222.11
111	B_1	9523.69	9503.08	9498.36	9497.16
121	B_1	10835.57	10624.35	10601.97	10575.05
201	B_1	11019.41	10940.46	10929.33	10958.65
003	B_1	11028.32	11016.65	11016.70	11012.56
211	B_1	12751.43	12018.75	11979.47	11997.56
013	B_1	12330.88	12067.49	12053.07	12051.01

The cluster operator in these cases is truncated at six boson.
The energies are in cm^{-1} unit.

states, we find that the NCCM results with six boson excitation operator are close to the full CI (maximum deviation is only $6\ cm^{-1}$ in case of $1_1 2_3$ state), although the values are not saturated at the six boson rank of the excitation operator. In case of the other higher energy excited states we find large deviations from the full CI values. However, as can be seen that these results improve dramatically on increasing the rank of the excitation operator from Ω_4 to Ω_5 to Ω_6. For example, the full CI energy of $2_2 3_2$ state is 10572.59 cm^{-1}. NCCM value with Ω_4 is $10926.89\ cm^{-1}$ which becomes $10791.43\ cm^{-1}$ with Ω_6.

Table 2.10: Comparision of CPU time

Molecule	Four boson	Five boson	Six boson	converged CI
H_2O	0.40s	0.43s	0.44s	3.94s

Table 2.11: Comparison of CPU time required for NCCM calculations with respect to the degree of freedoms of molecules

Molecule	CPU time
Tri-atomic (H_2O)	0.44s
Tetra-atomic (H_2CO)	9.69s

2.3.5 Computational time

The implicit assumption in the coupled cluster approach is that the higher order cluster operators converges rapidly. One can obtain the ground and excited state energies comparable to converged full CI accuracy with a lower order cluster and excitation operators. In the table 2.10, we present the comparison of converged full CI and NCCM with different level of truncation in excitation operator in terms of CPU time needed to do the calculations. All these calculations are done using Linux box (Intel 2.93 GB Core2Due).

We find that the time requirement for the CCM calculation is very little compared to the full CI calculations. We have seen from the variations of the excited state energies with respect to different level of approximations in the excitation operator that the most of the lower lying states are converged with Ω_6 and reached the converged full CI values. We find that our method is very efficient in terms of the CPU time required for the calculations and so it can be applied to study the vibrational energy spectra of molecules with higher degrees of freedoms. The CPU time required for tri atomic and tetra atomic molecules are presented in table 2.11. We used six boson approximation in both the cluster operator S and excitation operator Ω in this study.

2.4 Conclusion

In this work we have studied the convergence properties of the CCM/CCLRT approach in boson representation. In the two illustrative examples that we studied, we found the energy levels converge rapidly with respect to the cluster operator and they are almost saturated at S_4 level. The convergence for the excitation operator Ω is however slow. While the fundamentals are fairly well described by an excitation operator truncated as low as four boson level, the higher excited states have not always converged even at six boson level. This pattern has been observed earlier in the study of one dimensional anharmonic oscillator also. There are two possible sources for this inadequacy. As the level of excitation in a mode increases, the associated wave function samples larger region of space and hence feels affects of anharmonicity to a greater extent. The effects of such anharmonicity manifest themselves to first order in a shift of centroid of the wave function and in spreading of the wave function. Such displacement and/or squeezing are described exactly by exponential operators, as in the case for the wave function of a displaced harmonic oscillator. Depending on the magnitude of such effects the number of terms in the Taylor series expansion in the exponential would have to be large for a convergent result. It is for this reason that a low order expansion of the excitation operator is inadequate. This problem can be redressed by the use of a multi-reference coupled cluster description that can account for state specific displacement and squeezing.

A second source of inadequacy of the excitation operator comes from strong coupling between near resonance states that differ in the number of quanta of excitation among them. Since we are truncating the excitation operator based on the total number of quanta rather than on energetic criteria, the level density in the higher energy regime is underestimated, particularly when different groups of modes (such as stretching and bending) differ from each other significantly in their frequencies. Consequently states which fall in such regimes are not properly described.

Lastly, we turn to the utility of Arponen type of double similarity transformation. As

far as state energies are concerned, a second similarity transformation appears to have no significant advantage. However we found that some of the complex eigenvalues in the excitation spectrum have become real in the ECCM based calculations as we expected. It can be hoped that in the calculations of non-energetic properties, e.g. expectation values and transition matrix elements, this approach would be superior to the NCCM approach.

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Chapter 3

Effective Operator Approach Based on CCLRT to Calculate Vibrational Expectation Values and Transition Matrix Elements.

3.1 Introduction

In the second chapter we have discussed the formulation of the coupled cluster method to study the anharmonic vibrational spectra of polyatomic molecules in bosonic representation. The vibrational excited states are described using coupled cluster linear response theory [1–3] in which the excited states are obtained as the eigenvalues of the similarity transformed effective Hamiltonian H_{eff}^N

$$H_{eff}^N = e^{-S} H e^S. \tag{3.1}$$

As discussed in the previous chapter, the diagonalization of H_{eff}^N yields the transition energies as the eigenvalues. We studied the convergence pattern of the state energies with respect to different rank of cluster operator.

In this chapter, we turn our attention to the reliability of CCM approach for the calculation of properties other than state energies. Specifically, we study the convergence pattern of the CCM approach to the calculation of expectation values and transition matrix elements of the dipole moment operator. This is the first implementation of coupled cluster method to study the expectation values and transition matrix elements in the context of molecular vibrations. To the extent of our knowledge, no calculation on transition matrix elements is reported in literature using coupled cluster method even in electronic structure theory.

As discussed in the first chapter, the straight forward approach based on the CCM ansatz for the expectation is

$$
\begin{aligned}
\langle \hat{O} \rangle &= \frac{\langle 0|exp(S^{\dagger})\hat{O}exp(S)|0\rangle}{\langle 0|exp(S^{\dagger})exp(S|0\rangle} \\
&= \langle 0|exp(S^{\dagger})\hat{O}exp(S)|0\rangle_L.
\end{aligned}
\tag{3.2}
$$

The last expression is due to the linked cluster theorem [4, 5]. Unlike the equations for the cluster matrix elements, this equation is a non-terminating series even at any finite truncation of S and thus is impractical for the numerical work. Prasad [6] has earlier suggested an alternative approach for the calculation of expectation values and transition matrix elements within the CCM framework that bypasses the need to evaluate such infinite series. In this approach, these properties are calculated using effective operator which is a similarity transformation of the original operator

$$
\hat{O}_{eff} = exp(-S)\hat{O}exp(S).
\tag{3.3}
$$

In this chapter, we use this effective operator approach based on CCLRT to calculate vibrational expectation values and transition matrix elements. We study the convergence pattern of the expectation values and the transition matrix elements are studied as a function of the rank of the excitation operator. Since in the last chapter we have seen that the ground state cluster operator S converge rapidly, we keep it fixed at S_6 level throughout the study. The convergence pattern of the expectation values and the transition matrix elements are studied as a function of the rank of the excitation operator in CCLRT.

The similarity transformation of the Hamiltonian is at the heart of the CCM. Consequently, the H_{eff}^N is not manifestly Hermitian. This non-hermitian effective Hamiltonian generates on occasion complex eigenvalues. We use a double similarity transformation in the spirit of extended coupled cluster approach (ECCM) of Arponen [7–9] to recover the complex eigenvalues in an approximate way. Here, the ground state wave function is parametrized as

$$|\psi_g\rangle = e^S e^{-\sigma}|\phi_{ref}\rangle. \tag{3.4}$$

Here, the generator of the second similarity transformation σ consists of de-excitation operator alone. The effective Hamiltonian, H_{eff} is now hermitized up to first order. We noted in the previous chapter that this modification of the wave operator eliminates some of the complex eigenvalues. According to the Lie algebraic decoupling theorem, the equation of motion for S are decoupled from the σ matrix elements in the exact limit [6, 10]. In the NCCM based approach the ground state ket vector is exponentially parametrized but the ground state bra vector is linearly parametrized. However, in the ECCM based approach the ground state bra vector is also exponentially parametrized. Due to this, the ECCM based approach is expected to provide a better description for the calculations of these properties. The second goal of this chapter is to study the advantage of the ECCM over NCCM in calculating these properties.

The chapter is organized as follows. In the next section we describe the essential aspects of the calculation of expectation values and transition matrix elements from the CCM perspective. We have applied the formalism to water molecule and its isotopomers using an *ab inito* potential energy surface and dipole moment surface to understand the convergence properties of these quantities with respect to the truncation in the excitation operators. The results will be discussed in the next section. Finally we put concluding remarks.

3.2 Theory

It is recognized that the CCM approach involves the construction and diagonalization of an effective Hamiltonian after the similarity transformation in Eq. 3.1. It is possible to relate the left and right eigenvectors of H_{eff} to the eigenvectors of original Hamiltonian.

$$H_{eff}|R_i\rangle = E_i|R_i\rangle, \tag{3.5a}$$

$$\langle L_i|H_{eff} = \langle L_i|E_i, \tag{3.5b}$$

$$|\psi_i\rangle = N_i e^S|R_i\rangle, \tag{3.6a}$$

$$\langle\psi_i| = \langle L_i|e^{-S}M_i. \tag{3.6b}$$

By choosing the normalization constants M_i and N_i such that $M_i N_i\langle L_i|R_i\rangle = 1$, the expectation value of any arbitrary operator O is given by

$$\langle O\rangle = \langle\psi_i|O|\psi_i\rangle = \langle L_i|O_{eff}|R_i\rangle, \tag{3.7}$$

where,

$$O_{eff} = e^{-S}Oe^S. \tag{3.8}$$

These equations are identical to the equations derived by Z-vector[11, 12] or λ-vector[13] formalisms by earlier workers since all these method use a linearly parametrized left vector to calculate the expectation values. Similarly, the transition matrix elements between two states $|\psi_i\rangle$ and $|\psi_j\rangle$ are given by

$$|\langle\psi_i|O|\psi_j\rangle|^2 = \langle L_i|O_{eff}|R_j\rangle\langle L_j|O_{eff}|R_i\rangle, \tag{3.9}$$

and the phase of the transition matrix element $\phi(O_{ij} = |O_{ij}|e^{i\phi})$ is given by

$$\phi = \frac{1}{2}Im\big[ln(\langle L_i|O_{eff}|R_j\rangle/\langle L_j|O_{eff}|R_i\rangle)\big]. \tag{3.10}$$

We use this approach for the calculation of the expectation values and transition matrix elements of the dipole operator.

The structure of the equations remains unchanged in the case of ECCM. The only difference in the case of the ECCM is that the effective operators defined in Eq. 3.8 are replaced by

$$O_{eff} = e^{\sigma} e^{-S} O e^{S} e^{-\sigma}.$$ (3.11)

3.3   Results and Discussions:

We have applied the above discussed methodology of previous section to study the vibrational corrections to dipole moments of different vibrational states and transition matrix elements between ground state and several excited states of water molecule and isotopic variants HDO and D_2O. There are several accurate quartic *ab initio* potential energy surface (PES) available for these systems in the literature. However, there are very few dipole moment surfaces (DMS) reported in the literature. We have taken both PES and DMS from reference [14]. In addition to the calculation of the potential energy surface and dipole moment surface, these authors made extensive calculations to the dipole moment expectation values and transition matrix elements using perturbation theory. We choose both PES and DMS based on CISD calculations using STO basis for applying our methodology to H_2O, HDO and D_2O molecules. Although the potentials presented here are old, we chose these for consistency between PES and DMS in terms of basis set and method used in the electronic structure calculations. These potential energy surfaces do not contain the Coriolis coupling terms.

3.3.1 H_2O **Molecule:**

Over the years there have been extensive studies on the vibrational spectra of water molecule[15–17]. It is an archetypical local mode molecule because of large mass disparity between oxygen and hydrogen atoms. Moreover, the low barrier of inversion makes it highly anharmonic. Consequently, it is a very good test molecule for any theoretical method based on normal coordinate system. Since the goal of the present work is to

study the reliability of the effective operator approach based on coupled cluster linear response theory rather than attaining experimental accuracy, we compared our results with converged full CI results. As is well known, the quartic force field provides a poor description for the H_2O molecule[18]. Consequently, it does not give numbers that can be compared with experimental data even with full CI level. A higher order expansion in the potential is required to match experimental values. The present methodology can be easily expanded for higher order potential functions.

NCCM Based Calculation:

In the previous chapter we presented extensive calculations on the convergence of state energies with respect to the variation of the rank of both cluster operator S and excitation operator Ω from four boson to six boson level in NCCM and CCLRT respectively. We found that both the ground state and excited state energies have converged with respect to cluster operator by S_4 in NCCM. However, in some cases the results were not converged even with six boson rank of excitation operator Ω. Based on this, in present work we study the convergence pattern of the dipole operator expectation values and transition matrix elements with respect to rank of excitation operator Ω only. In all calculations we kept the cluster operator of NCCM fixed at six boson level. We compare our results with converged full CI results. For full CI we used 10-18-10 harmonic oscillator basis. Comparisons have also been made with the second order perturbation results of reference [14].

Expectation values of dipole operator

In table 3.1, we present the variation of expectation values of dipole operator with respect to truncation levels of excitation operator Ω keeping the cluster operator fixed at six boson level. The values presented in the table are vibrational corrections to the dipole moment. Z axis is taken as the molecular axis. The states with maximum three quanta excitations are reported here. We find that for the ground state and fundamentals, CCM

results are in excellent agreement with the converged full CI results. The values are converged even with as low as four boson excitation operator. For all states with two quanta of excitations, the dipole moment expectation values are very close to full CI values. In 200, 002 and 011 states the values are nearly converged with the rank of excitation operator. In case of 020, 030, 003 states, we find that dipole moment is monotonically converging with respect to excitation operator but have not saturated even at six boson level. For most of the three quantum states, the error is about 5% except for three states (120, 210 and 012) for which the maximum error is as high as 50%. As can be seen, the expectation values are not converged with respect to Ω even at six boson level. We find dramatic improvements in the dipole moment expectation values on increasing the rank of excitation operator from four boson to five boson to six boson in some cases. For example, dipole moment of 030 state changes from -7.07×10^{-2} Debye to -10.36×10^{-2} Debye from four boson to six boson rank of excitation operator. The converged full CI value for this state is -11.43×10^{-2} Debye. As we noted in the previous chapter that lower lying states like fundamentals, first overtones etc are well represented by CCLRT method because of its bi-variational nature. However, truncation of the linear excitation operator at six boson level does not describe the wave functions of higher states adequately. Convergence pattern of states energies also reflects these improper descriptions of the higher excited state wave functions. In table 3.1, we have compared the CCM dipole moment values with the second order perturbation theory results presented in reference [14] also. We found that for almost all states the CCM results are better than the second order perturbation results.

Table 3.1: variation of expectation values of dipole moment of H_2O with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.88	0.88	0.88	0.87	0.90
010	-2.09	-2.10	-2.10	-2.09	-1.93
020	-5.39	-5.62	-5.71	-5.87	4.80
100	2.26	2.26	2.26	2.26	2.32
030	-7.07	-9.17	-10.36	-11.43	-7.71
110	-0.31	-0.28	-0.29	-0.26	-0.47
120	-2.44	-2.81	-2.82	-3.41	-3.30
200	3.24	3.38	3.36	3.42	3.69
002	6.57	6.65	6.65	6.87	7.12
210	0.25	0.54	0.67	1.41	0.95
012	1.70	2.06	2.07	4.53	4.35
300	3.04	4.20	4.58	4.34	5.02
102	4.75	6.98	7.72	7.00	8.38
001	3.93	3.93	3.92	3.93	4.03
011	1.28	1.34	1.34	1.40	1.23
021	-1.72	-1.64	-1.55	-1.66	-1.61
101	4.67	4.84	4.83	4.88	5.37
111	1.32	2.35	2.63	2.60	2.61
201	3.90	5.48	5.87	5.52	6.66
003	6.83	9.13	9.59	9.75	10.17

[a] see reference [14].
The tabulated values are the vibrational corrections to the dipole moments ($\mu_{\nu\nu} - \mu_e$). Units are in 10^{-2} debye

Transition matrix elements

The absolute values of the transition matrix elements of H_2O from the ground state to different excited states are presented in table 3.2. Like state energies and dipole moment expectation values, here also we find excellent agreement between converged full CI and CCM with as low as four boson excitation operator for the fundamentals. Even for lower lying two quanta excited state 011 and three quanta excited state 111 we find that converged full CI values are reached by NCCM with four boson excitation operator. For two quanta states, the results are converged with the truncation of excitation operator and they are close to converged full CI values except in the cases where the transition

Table 3.2: Variation of absolute transition matrix elements of H_2O with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
010	14.75	14.75	14.76	14.75	14.6
020	0.58	0.57	0.57	0.73	0.93
100	3.59	3.59	3.59	3.59	3.50
030	0.16	0.18	0.19	0.07	–
110	0.10	0.10	0.10	0.06	0.22
200	0.44	0.44	0.44	0.35	0.44
002	0.08	0.07	0.08	0.01	0.08
012	0.13	0.13	0.13	0.02	–
300	0.02	0.01	0.03	0.09	–
102	0.11	0.11	0.11	0.03	–
001	6.27	6.27	6.27	6.26	6.60
011	1.62	1.62	1.62	1.64	3.10
021	0.06	0.06	0.05	0.07	–
101	0.94	0.94	0.94	0.78	1.10
111	0.34	0.35	0.35	0.32	–
201	0.08	0.10	0.11	0.07	–
003	0.14	0.14	0.13	0.07	–

[a] reference [14].

Values greater than 0.01 are reported.

matrix element is very small. In the study on energetics, we found that the ground state ket vector is well represented by as low as four body cluster operator S_4. So the errors in transition matrix elements must be due to inadequate description of ground state bra vector within NCCM approach. In NCCM approach the ground state bra vector is linearly parametrized. Paramatrizing the ground state bra vector by an exponential ansatz as is done in the ECCM approach aught to improve the transition matrix elements.

Finally, NCCM generally gives a better description for transition matrix elements than the second order perturbation theory.

ECCM Based Calculation:

In this section we compare the results of different levels of truncation of Ω operator after Arponen type of double similarity transformation. In all calculations both cluster operator S and σ are kept at six boson level.

Dipole Moment expectation values:

We present the variation of dipole moment expectation values for H_2O of with different levels of truncation of excitation operator with ECCM in table 3.3. Like energetics of the states, here also we find the improvement due to double similarity transformation over NCCM is marginal.

Transition Matrix elements:

Variation of the transition matrix elements with rank of excitation operator for H_2O are given in table 3.4. Here we find significant improvements due to the double similarity transformation of ECCM approach over NCCM. For fundamentals NCCM results are very close to converged full CI. So improvements due to ECCM over NCCM are marginal. Beyond the fundamental states, we find dramatic improvements with ECCM based calculations. For example, with NCCM based method the converged transition matrix element value for 020 state is 0.57×10^{-2} Debye , whereas the full CI value is

Table 3.3: varitation of expectation values of dipole moment of H_2O with varying excitation operator from four boson to six boson after Arponen type double similarity transformation.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.88	0.88	0.88	0.87	0.90
010	-2.03	-2.04	-2.04	-2.09	-1.93
020	-5.46	-5.58	-5.60	-5.87	-4.80
100	2.25	2.25	2.25	2.26	2.32
030	-7.10	-9.42	-10.18	-11.43	-7.71
110	-0.28	-0.29	-0.29	-0.26	-0.47
120	-2.44	-2.76	-2.87	-3.41	-3.30
200	3.37	3.37	3.38	3.42	3.69
002	6.62	6.64	6.64	6.87	7.12
210	0.26	0.69	0.73	1.41	0.95
012	1.71	2.11	2.18	4.53	4.35
300	3.03	4.41	4.49	4.34	5.02
102	4.66	7.19	7.69	7.00	8.38
001	3.90	3.90	3.90	3.93	4.03
011	1.32	1.35	1.35	1.40	1.23
021	-1.71	-1.64	-1.62	-1.66	-1.61
101	4.79	4.82	4.83	4.88	5.37
111	1.33	2.51	2.63	2.60	2.61
201	4.04	5.70	6.01	5.52	6.66
003	6.65	9.24	9.44	9.75	10.17

^{a} reference [14].

The tabulated values are the vibrational corrections to the dipole moments $(\mu_{\nu\nu} - \mu_e)$. Units are in 10^{-2} debye.

Table 3.4: Variation of absolute transition matrix elements of H_2O after Arponen type double similarity transformation with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
010	14.81	14.81	14.81	14.75	14.6
020	0.75	0.75	0.75	0.73	0.93
100	3.63	3.63	3.63	3.59	3.50
030	0.02	0.02	0.02	0.07	–
110	0.04	0.04	0.04	0.06	0.22
200	0.34	0.34	0.34	0.35	0.44
002	0.01	0.01	0.01	0.01	0.08
012	0.03	0.03	0.03	0.02	–
300	0.09	0.09	0.09	0.09	–
102	0.00	0.02	0.02	0.03	–
001	6.32	6.32	6.32	6.26	6.60
011	1.61	1.61	1.61	1.64	3.10
021	0.08	0.08	0.08	0.07	–
101	0.78	0.78	0.78	0.78	1.10
111	0.32	0.32	0.32	0.32	–
201	0.07	0.08	0.09	0.07	–
003	0.10	0.08	0.08	0.07	–

[a] reference [14].
Values greater than 0.01 are reported.

0.73×10^{-2} Debye. With ECCM based calculation it improves to 0.75×10^{-2} Debye. Similarly, for 002 state the full CI value is 0.01×10^{-2} Debye. NCCM based calculation gives 0.08×10^{-2} Debye whereas ECCM gives exact full CI value. Similarly, for 300, 101, 111 states we find exact full CI values with ECCM based method. In all the cases the errors by the ECCM based method are negligible. As we stated earlier, in the NCCM based method, the ground state bra vector is not properly described. In the ECCM the ground state bra vector is parametrized with an exponential operator. This makes ECCM approach significantly superior over NCCM in calculating transition matrix elements.

3.3.2 HDO **molecule:**

Our second case study is the HDO molecule. This isotopic variant of H_2O belongs to C_1 point group. We consider the molecule is in YZ plane. We have the dipole moment functions belong to both Y and Z directions. Unlike H_2O, here the vibrational modes are more local in nature. In H_2O, the two OH oscillators of same frequency strongly mixed to form the symmetric and antisymmetric normal modes. But in the case of HDO, the OD and OH are having different frequencies and consequently the resonance between the modes are less as comparative to H_2O molecule. In other words, the anharmonic coupling strengths are less in this molecule. For example, the force constant values of f_{133} in HDO is $-21.6 cm^{-1}$ as compared to $-305.6 cm^{-1}$ that in water. As a results, the CCM provides a better description for HDO molecule than for H_2O.

NCCM based calculations:

In this subsection we present the dipole moment expectation values and transition matrix elements of HDO molecule based on NCCM approach. We keep the cluster operator fixed at S_6 level and vary the excitation operator from four boson to six boson level. The results are compared with the converged full CI values. For CI calculations we use 10-18-10 harmonic oscillator basis set.

Table 3.5: Variation of expectation values of dipole moment of HDO molecule along Y direction with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.63	0.63	0.63	0.64	0.64
010	1.01	1.01	1.01	0.99	0.93
100	-0.47	-0.47	-0.47	-0.43	-0.51
020	1.44	1.43	1.42	1.36	1.31
001	2.51	2.51	2.51	2.53	2.79
110	-0.16	-0.17	-0.17	-0.15	-0.24
030	2.25	1.88	1.78	1.69	1.78
200	-1.24	-1.34	-1.33	-1.26	-1.62
011	2.99	2.96	2.95	2.96	1.85
120	0.38	0.17	0.12	0.10	0.12
101	1.41	1.42	1.42	1.48	1.64
021	4.68	3.41	3.05	3.14	3.33
210	-0.67	-1.10	-1.16	-1.07	-1.37
002	4.55	4.25	4.23	4.32	4.89
300	-0.63	-1.63	-1.91	-1.85	2.70
111	2.92	1.90	1.81	1.72	1.85
201	1.82	0.70	0.86	0.69	0.53
012	3.78	5.11	3.89	4.18	5.05
102	2.52	3.45	3.12	3.29	3.75

^{a} see reference [14].
The tabulated values are the vibrational corrections to the dipole moments ($\mu_{\nu\nu} - \mu_e$). Units are in 10^{-2} debye.

Dipole Moment expectation values:

In table 3.5 and table 3.6 we present the convergence pattern of dipole moment expectation values with respect to the different level of truncation of the excitation operator Ω for different vibrational states of HDO along Y and Z directions respectively. We find that the CCM dipole moment expectation values are excellent for the ground state and fundamentals along both Y and Z direction. The full CI values are reached by as low as four boson rank of the excitation operator. For the two quanta excited states the expectation values are fairly accurate with respect to converged full CI. In the case of three quanta excited states, we find deviations in the dipole moment expectation values. However, in these cases, the values are found to be converging monotonically with the

rank of the excitation operator. There are dramatic improvements in the dipole moment expectation values of three quanta excited states on increasing the rank Ω. For example, for $2_2 3_1$ state, the dipole moment expectation value along Z direction is 1.18×10^{-2} debye with Ω_4. With six boson excitation operator, it improves to -2.49×10^{-2} debye. The converged full CI value in this case is -2.96×10^{-2} debye. Similarly, for 2_3 state, dipole moment expectation value along Z direction changes from -4.31×10^{-2} debye to -6.27×10^{-2} debye from four boson to six boson excitation operator. The converged CI value is -6.64×10^{-2} debye. These results support the speculation that to attain the accuracy of dipole moment expectation values of higher excited states comparable to the full CI values, one should go for higher rank of excitation operator. NCCM generally gives a better description than the second order perturbation theory.

Table 3.6: Variation of expectation values of dipole moment of HDO molecule along Z direction with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.71	0.71	0.71	0.70	0.75
010	-1.62	-1.63	-1.63	- 1.63	-1.80
100	2.10	2.09	2.09	2.13	2.34
020	-3.42	-3.59	-3.65	-3.77	-4.41
001	2.02	2.03	2.03	2.03	3.17
110	-0.16	-0.18	-0.19	-0.15	-0.21
030	-4.31	-5.54	-6.27	-6.64	-7.09
200	3.21	3.32	3.32	3.39	3.89
011	-0.51	-0.69	-0.83	-0.77	0.73
120	-1.82	-2.13	-2.18	-2.41	-2.82
101	3.55	3.62	3.65	3.64	4.75
021	1.18	-1.24	-2.49	-2.96	-1.77
210	0.44	0.65	0.69	1.15	1.34
002	2.95	3.29	3.52	3.41	5.51
300	2.95	4.16	4.59	4.45	5.39
111	1.87	1.22	1.17	0.44	2.32
201	2.06	4.63	4.39	4.48	6.30
012	0.59	2.78	-1.11	-3.66	3.18
102	4.09	4.45	5.05	5.40	7.09

[a] see reference [14].
The tabulated values are the vibrational corrections to the dipole moments ($\mu_{\nu\nu} - \mu_e$). Units are in 10^{-2} debye.

Transition matrix elements:

The absolute values of the transition matrix elements of HDO molecule from the ground state to different excited states along Y and Z directions are presented in table 3.7 and table 3.8 respectively. Along Y axis, for the most of the states up to three quanta excitations, the transition matrix elements are in excellent agreement with the converged full CI results. Along Z direction, for the fundamentals and lower lying two quanta excited states 2_2, $1_1 2_1$, $1_1 3_1$ and even some of the three quanta excited states e.g. 1_3, $1_2 3_1$, $1_1 3_2$ the transition matrix elements are very close to the full CI values. However, in some of the higher energy states, we find the deviations in the transition matrix elements in comparison to full CI values. Like the case of H_2O molecule, here also we observe

Table 3.7: Variation of absolute transition matrix of HDO molecule with varying excitation operator.

State	4 boson	5 boson	6 boson	Full CI
010	3.58	3.58	3.58	3.93
100	3.82	3.82	3.82	3.79
020	1.38	1.35	1.35	1.38
001	4.78	4.79	4.79	4.80
110	0.91	0.91	0.91	0.91
030	0.47	0.46	0.45	0.47
200	0.57	0.57	0.57	0.48
011	0.98	0.99	1.00	1.00
120	0.03	0.03	0.03	0.04
101	0.10	0.10	0.10	0.10
210	0.17	0.17	0.17	0.13
021	0.11	0.41	0.41	0.32
002	0.58	0.66	0.69	0.57
300	0.07	0.07	0.07	0.07
111	0.01	0.01	0.01	0.02
012	0.19	0.19	0.19	0.17
201	0.01	0.03	0.02	0.03
102	0.01	0.01	0.01	0.01

Units are in 10^{-2} debye:dipole moment along Y direction.
Values greater than 0.01 are reported.

Table 3.8: Variation of absolute transition matrix of HDO molecule with varying excitation operator.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
010	13.66	13.66	13.66	13.75	13.6
100	2.43	2.43	2.43	2.50	2.50
020	1.34	1.32	1.32	1.42	0.31
001	2.22	2.23	2.23	2.21	2.50
110	0.07	0.07	0.07	0.06	0.14
030	0.14	0.15	0.16	0.02	–
200	0.22	0.22	0.22	0.15	0.19
011	0.12	0.12	0.13	0.05	0.32
120	0.06	0.06	0.06	0.02	–
101	0.11	0.11	0.11	0.13	0.26
210	0.09	0.09	0.09	0.02	–
021	0.04	0.21	0.19	0.13	–
002	0.27	0.22	0.24	0.16	0.23
300	0.04	0.05	0.05	0.05	–
201	0.01	0.01	0.01	0.01	–
102	0.01	0.01	0.01	0.01	–

[a] see reference [14].
Units are in 10^{-2} debye:dipole moment along Z direction.
Values greater than 0.01 are reported.

that the transition matrix elements are converged with respect to the rank of the excitation operator although they did not reach the full CI values for some states. As stated earlier, since the ground state ket vector is well represented by as low as S_4 cluster operator, the errors in the transition matrix elements are due to linearly parametrization of the ground state bra vector in NCCM approach.

We note that the NCCM description of the transition matrix element are better than the second order perturbation values.

ECCM based calculations:

Here we present the results of different levels of truncation of Ω operator based on ECCM calculations. We compare these values with converged full CI results. In all these calculations, both the cluster operator S and σ are kept at the six boson level.

Table 3.9: Variation of expectation values of dipole moment of HDO molecule along Y direction with varying excitation operator from four boson to six boson after Arponen type double similarity transformation.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.63	0.63	0.63	0.64	0.64
010	1.02	1.02	1.02	0.99	0.93
100	-0.46	-0.46	-0.46	-0.43	-0.51
020	1.45	1.45	1.44	1.36	1.31
001	2.49	2.49	2.49	2.53	2.79
110	-0.15	-0.15	-0.15	-0.15	-0.24
030	2.24	1.88	1.82	1.69	1.74
200	-1.31	-1.31	-1.31	-1.26	-1.62
011	3.06	2.96	2.94	2.96	3.02
120	0.39	0.19	0.18	0.10	0.12
101	1.43	1.43	1.43	1.48	1.64
021	4.70	3.52	3.13	3.14	3.33
210	-0.64	-1.16	-1.19	-1.07	-1.37
002	4.65	4.25	4.20	4.32	4.89
300	-0.47	-1.86	-1.88	-1.85	2.70
111	2.96	1.97	1.84	1.72	1.85
201	1.85	0.65	0.72	0.69	0.53
012	3.81	5.25	4.19	4.18	5.05
102	2.52	3.60	3.26	3.29	3.75

[a] see reference [14].
The tabulated values are the vibrational corrections to the dipole moments ($\mu_{\nu\nu} - \mu_e$). Units are in 10^{-2} debye.

Dipole Moment Expectation values:

The variations of dipole moment expectation values of HDO molecule with different levels of truncation of the excitation operator with ECCM along Y and Z direction are given respectively in table 3.9 and table 3.10. Like H_2O molecule, here also we find the improvement due to double similarity transformation over NCCM is marginal.

Transition Matrix Elements:

The variations of the transition matrix elements from the ground state to different excited states with the rank of the excitation operator Ω along Y and Z axis are given

Table 3.10: Variation of expectation values of dipole moment of HDO molecule along Z direction with varying excitation operator from four boson to six boson after Arponen type double similarity transformation.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.71	0.71	0.71	0.70	0.75
010	-1.59	-1.59	-1.59	- 1.63	-1.80
100	2.10	2.10	2.10	2.13	2.34
020	-3.48	-3.55	-3.56	-3.77	-4.41
001	1.99	1.98	1.98	2.03	3.17
110	-0.14	-0.16	-0.16	-0.15	-0.21
030	-4.40	-5.74	-6.14	-6.64	-7.09
200	3.33	3.32	3.31	3.39	3.89
011	-0.48	-0.74	-0.86	-0.77	0.73
120	-1.85	-2.16	-2.24	-2.41	-2.82
101	3.59	3.60	3.60	3.64	4.75
021	1.18	-0.97	-2.31	-2.96	-1.77
210	0.42	0.79	0.82	1.15	1.34
002	3.12	3.10	3.22	3.41	5.51
300	2.90	4.47	4.58	4.45	5.39
111	1.86	1.27	1.15	0.44	2.32
201	2.08	4.73	4.39	4.58	6.30
012	2.2	2.92	-0.74	-3.66	3.18
102	4.12	4.37	4.97	5.40	7.09

[a] see reference [14].

The tabulated values are the vibrational corrections to the dipole moments ($\mu_{\nu\nu} - \mu_e$). Units are in 10^{-2} debye.

Table 3.11: Variation of absolute transition matrix of HDO molecule after Arponen type of double similarity transformation with varying excitation operator.

State	4 boson	5 boson	6 boson	Full CI
010	3.60	3.60	3.60	3.93
100	3.84	3.84	3.84	3.79
020	1.43	1.43	1.43	1.38
001	4.80	4.80	4.80	4.80
110	0.90	0.90	0.90	0.90
030	0.51	0.49	0.48	0.47
200	0.49	0.49	0.49	0.48
011	0.97	0.98	0.98	1.00
120	0.04	0.04	0.04	0.04
101	0.10	0.10	0.10	0.10
210	0.13	0.12	0.12	0.12
021	0.13	0.36	0.33	0.32
002	0.48	0.52	0.54	0.57
300	0.08	0.08	0.08	0.07
111	0.001	0.01	0.01	0.02
012	0.19	0.20	0.18	0.17
201	0.03	0.01	0.04	0.03

Units are in 10^{-2} debye:dipole moment along Y direction.
Values greater than 0.01 are reported.

Table 3.12: Variation of absolute transition matrix of HDO molecule after Arponen type of double similarity transformation with varying excitation operator.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
010	13.71	13.71	13.71	13.75	13.6
100	2.46	2.46	2.46	2.50	2.50
020	1.47	1.47	1.47	1.42	0.31
001	2.21	2.21	2.21	2.21	2.50
110	0.07	0.07	0.07	0.06	0.14
030	0.01	0.00	0.00	0.02	–
200	0.14	0.14	0.14	0.15	0.19
011	0.04	0.04	0.04	0.05	0.32
120	0.00	0.00	0.00	0.02	–
101	0.13	0.12	0.12	0.13	0.26
210	0.01	0.00	0.01	0.02	–
021	0.08	0.15	0.15	0.13	–
002	0.18	0.14	0.14	0.16	0.23
300	0.06	0.06	0.06	0.05	–
201	0.00	0.01	0.01	0.01	–
102	0.01	0.01	0.01	0.01	–

^{a} see reference [14].
Units are in 10^{-2} debye.:dipole moment along Z direction.
Values greater than 0.01 are reported.

respectively in table 3.11 and table 3.12. We find significant improvements in the transition matrix elements due to double similarity transformation of ECCM approach in the cases where we get deviations with the NCCM based approach. For example, with the NCCM based calculation the transition matrix element value for the $2_1 3_1$ state along Z axis is 0.13×10^{-2} debye which appears to be converged with the rank of the excitation operator. The converged full CI value is 0.05×10^{-2} debye. With the ECCM based calculation this value improves to 0.04×10^{-2} debye. The values of the transition matrix elements support our speculation that due to exponential parametrization of the ground state bra vector the transition matrix elements are better represented by the ECCM based approach than by NCCM based approach.

3.3.3 D_2O

Our next case study is the D_2O molecule. This isotopic variant of water molecule is comparatively less anharmonic than H_2O due to the presence of heavier terminal atom and consequently, the CCM provides more accurate description. We perform both NCCM based and ECCM based calculations compare the results with the converged full CI. For full CI calculations we used 10-18-10 harmonic oscillator basis functions. The Z axis is taken as the molecular axis. The states with maximum three quanta excitations are reported here.

NCCM Based Calculations:

We present the convergence pattern of the dipole moment expectation values and transition matrix elements with respect to the rank of the excitation operator Ω in CCLRT. We kept the ground state cluster operator fixed at S_6 level.

Dipole Moment Expectation Values:

The expectation values of dipole moment operator at different levels of approximation in the excitation operator Ω in CCLRT for D_2O molecule are given in table 3.13. We find that for the ground state and the fundamentals the converged CI values are obtained with as low as four boson rank of the excitation operator. For the states up to two quanta excitations, the results attain the full CI accuracy with six boson excitation operator. Even for some of the lower lying three quanta excited states (2_3, 1_3, $1_1 3_2$ and $1_1 2_1 3_1$), we find very accurate results with the six boson operator. For other three quanta excited states, we get deviation in the dipole moment expectation values in compare to converged full CI results. However, values are monotonically converging with the rank of the excitation operator. We find that these deviations are less in comparison to H_2O molecule.

Table 3.13: variation of expectation values of dipole moment of D_2O with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.71	0.71	0.71	0.70	0.72
010	-1.37	-1.37	-1.37	-1.37	-1.29
020	-3.61	-3.71	-3.74	-3.79	-3.32
100	1.60	1.60	1.60	1.59	1.62
030	-5.07	-6.13	-6.62	-6.76	-5.37
110	-0.32	-0.31	-0.31	-0.30	-0.37
120	-1.73	-2.08	-2.11	-2.52	-2.37
200	2.30	2.40	2.40	2.43	2.49
002	5.34	5.39	5.39	5.53	5.73
210	0.45	0.48	0.56	0.74	0.53
012	1.89	2.15	2.17	3.85	3.76
300	1.25	2.88	3.14	3.14	3.34
102	3.98	5.57	6.04	6.03	6.53
001	3.17	3.17	3.17	3.17	3.24
011	1.28	1.32	1.32	1.35	1.25
021	-0.84	-0.76	-0.72	-0.76	-0.77
101	3.72	3.83	3.84	3.87	4.09
111	1.32	2.04	2.22	2.20	2.12
201	2.81	4.34	4.67	4.42	4.91
003	6.19	7.43	7.67	7.83	8.19

[a] see reference [14].
Units are in 10^{-2} debye. The tabulated values are the vibrational corrections to the dipole moments ($\mu_{\nu\nu} - \mu_e$).

Table 3.14: Variation of absolute transition matrix elements of D_2O with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
010	12.53	12.53	12.53	12.53	12.4
020	0.60	0.60	0.60	0.71	0.83
100	3.56	3.56	3.56	3.56	3.50
030	0.10	0.11	0.11	0.04	–
110	0.07	0.07	0.07	0.02	0.15
120	0.02	0.02	0.02	0.02	–
200	0.37	0.37	0.38	0.30	0.35
002	0.04	0.03	0.04	0.02	0.03
012	0.09	0.10	0.10	0.02	–
300	0.05	0.04	0.05	0.06	–
102	0.07	0.07	0.07	0.03	–
001	5.48	5.48	5.48	5.47	5.30
011	1.23	1.23	1.23	1.23	2.30
021	0.09	0.08	0.08	0.09	–
101	0.76	0.76	0.76	0.64	0.82
111	0.22	0.23	0.21	0.20	–
201	0.06	0.07	0.08	0.07	–
003	0.09	0.09	0.09	0.04	–

[a] see reference [14].
Values greater than 0.01 are reported.

Transition Matrix Elements:

The transition matrix elements of D_2O molecule from the ground state to different excited states with different truncations of the Ω operator are presented in table 3.14. Like the case of H_2O and HDO, the CCM gives excellent results for the fundamental states. Even for some two quanta excited states, the CCM results are fairly good in comparison with converged CI values. However, for higher energy states we find deviations between CCM values and full CI values although the NCCM values are converged with the rank of the excitation operator. This is, as we stated earlier, due to improper parametrization of the ground state bra vector in the NCCM based calculations.

ECCM Based Calculations:

In the ECCM based calculations we kept both the cluster operator S and σ fixed at six boson level.

Dipole Moment Expectation Values:

We present the convergence pattern of the dipole moment expectation values after Arponen type double similarity transformation in the ECCM based calculations in table 3.15. Like the case of the H_2O and HDO molecules, here also we find the improvements of the dipole moment expectation values due to ECCM based approach over NCCM are marginal.

Transition Matrix Elements:

The variations of the transition matrix elements of D_2O molecule with varying excitation operator from four boson to six boson are presented in table 3.16. Since for the fundamentals the NCCM values are close to the full CI, the improvement due to double similarity transformation in ECCM is marginal. However, for other states we find that the

Table 3.15: variation of expectation values of dipole moment of (D_2O) after Arponen type of double similarity transformation with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
000	0.71	0.71	0.71	0.70	0.72
010	-1.34	-1.34	-1.34	-1.37	-1.29
020	-3.65	-3.69	-3.69	-3.79	-3.32
100	1.59	1.59	1.59	1.59	1.62
030	-5.09	-6.25	-6.50	-6.76	-5.37
110	-0.30	-0.31	-0.32	-0.30	-0.37
120	-1.73	-2.05	-2.14	-2.52	-2.37
200	2.38	2.39	2.39	2.43	2.49
002	5.37	5.38	5.38	5.53	5.73
210	0.46	0.57	0.58	0.74	0.53
012	1.90	2.18	2.22	3.85	3.76
300	1.32	3.06	3.11	3.14	3.34
102	3.93	5.70	6.00	6.03	6.53
001	3.16	3.16	3.16	3.17	3.24
011	1.30	1.31	1.32	1.35	1.25
021	-0.83	-0.76	-0.75	-0.76	-0.77
101	3.80	3.83	3.83	3.87	4.09
111	1.34	2.14	2.21	2.20	2.12
201	2.81	4.51	4.77	4.42	4.91
003	6.16	7.48	7.58	7.80	8.19

[a] see reference [14].
The tabulated values are the vibrational corrections to the dipole moments $(\mu_{\nu\nu} - \mu_e)$.
Units are in 10^{-2} *debye*

Table 3.16: Variation of absolute transition matrix elements of D_2O after Arponen type of double similarity transformation with varying excitation operator from four boson to six boson.

State	4 boson	5 boson	6 boson	Full CI	$PT2^a$
010	12.56	12.56	12.56	12.53	12.4
020	0.71	0.72	0.72	0.71	0.83
100	3.58	3.59	3.59	3.56	3.50
030	0.01	0.01	0.01	0.04	–
110	0.01	0.01	0.01	0.02	0.15
120	0.04	0.04	0.04	0.02	–
200	0.29	0.29	0.29	0.30	0.35
002	0.02	0.02	0.02	0.02	0.03
012	0.02	0.02	0.02	0.02	–
300	0.05	0.06	0.06	0.06	–
102	0.01	0.01	0.01	0.03	–
001	5.51	5.51	5.51	5.47	5.30
011	1.21	1.21	1.21	1.23	2.30
021	0.09	0.09	0.09	0.09	–
101	0.76	0.76	0.64	0.64	0.82
111	0.21	0.21	0.21	0.20	–
201	0.07	0.08	0.08	0.07	–
003	0.05	0.05	0.05	0.04	–

^{a} see reference [14].

Values greater than 0.01 are reported.

NCCM values are converged with respect to the rank of the excitation operator, although they are away from the full CI values. The double similarity transformation in ECCM approach improves the results significantly. For example, with the NCCM based method, the converged absolute transition matrix element value from ground state to $1_1 2_1$ state is 0.07×10^{-2} debye, which is quite away from the converged full CI value 0.02×10^{-2} debye. With ECCM based calculation, it improves to 0.01×10^{-2} debye. Similarly, for the $2_1 3_2$ state the full CI value is 0.02×10^{-2} debye. The NCCM based calculation gives 0.10×10^{-2} debye, whereas ECCM based calculation gives the exact full CI value.

3.4   Conclusion

In this work, we presented an effective operator approach within the framework of CCM to calculate expectation values of operators and absolute transition matrix elements. We conclude that these properties can be calculated very accurately using CCLRT. We studied the convergence pattern of these properties with respect to truncations of excitation operator in CCLRT. We found that for fundamentals and most of the states with two quanta excitations these properties are converged with the rank of excitation operator and reached full CI limit by Ω_4. For higher states, the values tend to approach full CI values on going from four boson to six boson rank of excitation operator.

Next, we turn to the utility of Arponen type of double similarity transformation. We found that the ECCM does not offer any significant advantage over NCCM as far as state energies and expectation values are concerned. However, the story is quite different in case of transition matrix elements. Here, the ECCM fares far better than the NCCM, particularly when the transition matrix elements are small.

The CCLRT approach with a low rank excitation operator does not appear to be suitable for the description of highly excited states. As the number of quanta of excitation in a molecule increases, the wave function samples larger region of coordinate space, and consequently, are affected to a greater extent by the anharmonicity. This has some

intriguing consequences on the wave functions. For example, in a system described by quartic potential, the centroid of the wave functions would move away from the origin in the energy regime dominated by cubic terms of the potential, but would return towards the origin as the quartic term becomes significant at higher energies. Thus a proper description of the shifting of the wave function centroids and changes in their effective frequencies is necessary to describe such states. The CCLRT, with its linear structure, is perhaps not the best way to parametrize such changes. A multi-reference CCM for the excited states that describe the shifts in the centroids and frequencies in a state specific manner might provide a better description. The multi-reference coupled cluster formalism in bosonic representation is presented in the next chapter.

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Chapter 4

Formulation of vibrational multi-reference coupled cluster theory

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4.1 Introduction

The coupled cluster studies on vibrational systems discussed so far use coupled cluster linear response theory (CCLRT) to describe the excited states. In the previous chapters we have seen that the CCLRT provides fairly good descriptions of the ground state and lower lying states with six boson rank of the cluster as well as the excitation operator. However, it is well knowen that the limited CCLRT is not size consistent. In addition, the CCLRT with its linear structure, coupled to a low rank truncation is not adequate for the higher excited states. We speculated that the wave functions of the higher excited states sample larger region of space and hence the effect of anharmonicity is greater in this region. The effects of such anharmonicity manifest themselves to first order in a shift of the centroid of the wave functions and in the spreading of the wave functions. Hence a state selective description of the shifting of centroid of the wave function, i.e.

the expectation values of the normal coordinates ($< Q_i >$), and spreading of the wave functions i.e. width of the function is required. The single reference based CCM does not give state specific displacements. To illustrate, let us consider the unitary operator

$$U_q^0 = e^{S(a^\dagger - a)}. \tag{4.1}$$

It can be shown easily that U_q^0 operator displaces the centroid of wave function of all states by $\sqrt{2}S$,

$$\langle \phi_k | U_q^{0^{-1}} q U_q^0 | \phi_k \rangle = \sqrt{2}S, \tag{4.2}$$

when the harmonic oscillator basis functions ϕ_k are centred at the origin. Similarly, it can be shown that the unitary operator

$$U_{qq}^0 = e^{S(a^{\dagger 2} - a^2)} \tag{4.3}$$

scales the coordinates q. These displacements and/or scaling are independent of ϕ_k used to evaluate the expectation values. The coupled cluster ansatz at two boson level is the normally ordered form of these unitary operators U_q^0 and U_{qq}^0. Consequently, the NCCM ansatz gives the displacements for the ground state correctly. However, it does not reflect the state specific displacements present in the molecular vibrational wave functions. Since for higher energy states the state specific descriptions of the displacements of normal coordinates becomes more important, the CCLRT with its linear operator is not adequate to describe these states correctly.

An alternative approach to describe the excited states within coupled cluster framework is the multireference coupled cluster method (MRCCM)[1–11] based on effective Hamiltonian theory. As mentioned in the first chapter, the valance-universal version of the MRCCM or variously known as the Fock Space multi-reference coupled cluster method (FS-MRCCM) [2–11] has been used successfully for the description of the excitation energies of electronic structure theory of atoms and molecules. In the FS-MRCCM along with the normally ordered U_q^0 and U_{qq}^0 operators, the wave operator includes the following unitary operator,

$$U_q^1 = e^{S(a^{\dagger 2} a - a^\dagger a^2)}. \tag{4.4}$$

The expectation values of q with U_q^1 operator is,

$$\langle\phi_k|U_q^{1^{-1}}qU_q^1|\phi_k\rangle = 2\sqrt{2k}S + \sqrt{2k}S^2 + \dots. \tag{4.5}$$

This expectation value has linearly dependent displacement terms to the leading order on the wave number k. In other word, it accounts for the displacement of the centroid of the wave functions depending on the wave number k. Consequently, it is expected to provide a better description for the higher energy states.

The basic approach of a multi-reference method is to define an effective Hamiltonian in a low dimensional model space or P space, whose eigenvalues are equal to the some of the desirable eigenvalues of the physical Hamiltonian. The effect of the complementary space (Q space) is taken into account in the construction of the effective Hamiltonian by using a wave operator (Ω). The wave operator, as defined earlier, generates the exact functions by its action on the model space functions

$$|\Psi_k\rangle = \Omega|\Psi_k^0\rangle. \tag{4.6}$$

There are two different type of MRCC approaches studied extensively in the literature. These two approaches differ in the form of the wave operator. One is the Hilbert space MRCC method (HSMRCCM) [1], where the wave operator contains different cluster operators for different functions in the model space and each function acts as vacuum. The second approach is the Fock space MRCC method (FS-MRCCM) which is based on the concept of common vacuum. In FS-MRCCM, a valence universal wave operator of the type,

$$\Omega = e^{S^0}e^{S^1}e^{S^2}\dots \tag{4.7}$$

is used to map the reference state to the corresponding correlated states. Here, the wave operator includes, in addition to cluster operator S^0 which is similar to NCCM cluster operator, additional S^i operators that induces excitations from the model space P^i. The cluster operator S^i consists of i number of annihilation operators along with at least $i+1$ number of creation operators. As a consequence, they do not commute. Due to non-commuting nature of the cluster operators, the resulting equations to evaluate the cluster

matrix elements are fully coupled. Mukherjee and co-workers [4, 12] and Lindgren [2] proposed a de-coupling scheme of the cluster operators which is known as subsystem embedding condition (SEC) to evaluate the cluster matrix elements. According to this, the cluster operators corresponding to a lower particle system is decoupled from the higher particle system. Later on, Haque and Mukherjee [13] showed that this decoupling holds rigorously when the cluster operators are expressed in normal ordered form. However, using Lie algebraic arguments Sree Latha and Prasad [14] showed that the SEC holds in general for a complete model space.

Once the wave operator is defined, the effective Hamiltonian is constructed by the similarity transformation of the Hamiltonian within the model space,

$$H_{eff} = P\Omega^{-1}H\Omega P. \tag{4.8}$$

The cluster operators are obtained from the equation

$$QH_{eff}P = 0. \tag{4.9}$$

Use of SEC greatly reduces the computational efforts to solve this equation. The exact energies are obtained by diagonalizing the effective Hamiltonian H_{eff} in the P space.

In this chapter we aim to develop the multireference coupled cluster method in the line of electronic structure theory to describe the vibrational excited states of molecule in bosonic representation. This chapter is organized as follows. In the next section we discuss the formulation and features of the FS-MRCC approach in bosonic representation. Next, we present some results of the implementation of vibrational FS-MRCC method for the fundamental states of molecules. Finally some concluding remarks are given.

4.2 Theory

At the out set, we define the notations and certain definitions. We take the optimized Hartree product as the vacuum. Since in the bosonic representation the excitations are

defined in terms of quanta of energy rather than the physical particle, we define the model space accordingly. For example, all the one quanta excited states i.e. the fundamental states define a model space. We denote the corresponding model space by the notation M_1. Similarly, the states with two quanta excitations from the vacuum define another model space denoted by M_2 and so on. In Fock space notation, we designate by $\Psi_i^{0(m)}$ a function from the model space of m quanta excited states. For the fundamentals, the model space is written as

$$|\Psi_i^{0(1)}\rangle = \sum_\mu C_{\mu i}^1 |\phi_\mu^1\rangle. \tag{4.10}$$

The model space functions are generated by the actions of the creation operators on the vacuum. For example, action of one creation operator on the vacuum generates a function in the fundamental model space M_1. Similarly, action of two creation operators generates the function of the M_2 model space,

$$a_\mu^\dagger |0\rangle = |\phi_\mu^1\rangle, \tag{4.11}$$

$$a_\mu^\dagger a_\nu^\dagger |0\rangle = |\phi_{\mu\nu}^{11}\rangle, \tag{4.12}$$

and so on. In such kind of model spaces all the functions are occupied in all possible manner and hence they are inherently complete. Now, we define the form of the wave operator Ω. To generate the exact state of m quanta excitations, the wave operator must generate all possible valid excitations from the model space. For example, the model space of the fundamentals, in addition to the single reference cluster operators which contains only the creation operators (designated by S^0), the wave operator must contain the cluster operator that is able to destroy one quantum in the model space. That is in the diagrammatic representation of these operators, there should be one annihilation line along with the creation lines. This additional cluster operator is designated by S^1. Like S^0, the S^1 operator also splits into various n-body excitation operators depending upon the rank of excitations from the model space

$$S^1 = \sum_{n=2}^{\infty} S_{n1}^1, \tag{4.13}$$

136

where S_{n1} consists of n quanta excitation operators and one de-excitation operator. The sum in the above expression excludes 1 since such kind of cluster operators generate a lower or present model space function by its action on the current model space function. The form of S_{21}^1 operator is given by,

$$S_{21}^1 = \sum_{i \leq j} \sum_k S_{ijk}^1 a_i^\dagger a_j^\dagger a_k. \tag{4.14}$$

So, the form of the wave operator for the model space of the fundamentals is given by,

$$\Omega = e^{S^0} e^{S^1}. \tag{4.15}$$

Similarly, for the model space with two quanta excitations, we must have another set of cluster operator S^2 which must contain two annihilation operators and at least three creation operators to generate a valid excitation,

$$S^2 = \sum_{n=3}^{\infty} S_{n2}^2. \tag{4.16}$$

In general, for a problem, for which the model space consists of m quanta excitations, the cluster operator must be able to destroy m quanta. Hence the wave operator is defined by

$$\Omega = e^{S^0} e^{S^1} e^{S^2} \dots e^{S^m}. \tag{4.17}$$

Now, the Schrödinger equation for the manifold of states is written as,

$$H|\Psi_i^m\rangle = E_i|\Psi_i^m\rangle, \tag{4.18}$$

which leads to

$$H\Omega\left(\sum_i C_{i\mu}^m \phi_i^m\right) = E_\mu \Omega\left(\sum_i C_{i\mu}^m \phi_i^m\right) \tag{4.19}$$

where, ϕ_i^m are the functions in the model space.

Now, we define the effective Hamiltonian for the m quanta excited states as

$$H_{eff}^m = P^m \Omega^{-1} H \Omega P^m, \tag{4.20}$$

that is

$$(H^m_{eff})_{ij} = \langle \phi^m_i | \Omega^{-1} H \Omega | \phi^m_j \rangle. \tag{4.21}$$

Here, P^m is the projection operator onto the model space defined by

$$P^m = \sum_i | \phi^m_i \rangle \langle \phi^m_i |. \tag{4.22}$$

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

$$Q^m = 1 - \sum_{k=0}^{m} P^k. \tag{4.23}$$

The FS-MRCC equations for the cluster amplitudes are obtained by solving the equations

$$Q^m \Omega^{-1} H \Omega P^m = 0. \tag{4.24}$$

Introducing the form of Ω in Eq. 4.24 we get,

$$Q^m e^{-S^m} ... e^{-S^2} e^{-S^1} e^{-S^0} H e^{S^0} e^{S^1} e^{S^2} .. e^{-S^m} P^m = 0. \tag{4.25}$$

The Eq. 4.25 represents a set of coupled nonlinear equations for the cluster operators of different sectors. As mentioned in the introduction, the lower sector cluster amplitudes are decoupled from the higher sector cluster amplitudes due to subsystem embedding condition. The equations for the different cluster amplitudes are solved from lower sector to higher sectors successively. That is, first the equations for the zero valance sector is solved to obtain S^0 cluster amplitudes from

$$Q^0 e^{-S^0} H e^{S^0} p^0 = 0. \tag{4.26}$$

Using S^0, the effective Hamiltonian H^1_{eff} is constructed as

$$H^1_{eff} = e^{-S^0} H e^{S^0}. \tag{4.27}$$

The matrix elements of the S^1 cluster operator are obtained by solving the equations for the P^1 sector

$$Q^1 e^{-S^1} H^1_{eff} e^{S^1} P^1 = 0. \tag{4.28}$$

In the similar way the effective Hamiltonian for the next sector is constructed using S^1 and H_{eff}^1 and equations for the corresponding cluster operators are solved. This way the equations for the higher sector cluster matrix elements are obtained by using the lower sector cluster operators elements successively.

4.3 Results and Discussions

In this study we have implemented the above discussed methodology to study the fundamental vibrational states. The model space consists of one quanta excited states. For the sake of simplicity of calculations, the S^1 cluster is truncated at four boson level. That is, the S^1 operator is having maximum three excitation operators and one de-excitation operator. The results are presented below.

4.3.1 Truncated Morse Oscillator

Our first case study is one dimensional anharmonic oscillator with truncated Morse potential. The Morse potential is given by

$$V_{Morse} = D(1 - e^{\alpha x})^2. \tag{4.29}$$

Here, D is the dissociation energy of the Morse oscillator and α is a parameter. Expanding the expression in Eq. 4.29 and truncating the infinite series at fourth order in x one get the form of the potential,

$$V_T = D(\alpha^2 x^2 - \alpha^3 x^3 + \frac{7}{12}\alpha^4 x^4). \tag{4.30}$$

The relation between α and the dissociation energy D is given by

$$\alpha = \frac{\omega_e}{\sqrt{2D}}, \tag{4.31}$$

where, ω_e is the frequency of the oscillator at equilibrium.

Table 4.1: Energy of truncated Morse Oscillator at different D values.

D value	CCLRT	MRCC	Full CI
15	0.9715	0.9714	0.9715
20	0.9777	0.9776	0.9776
25	0.9817	0.9817	0.9816

Putting the relation of Eq. 4.31 in Eq. 4.30 we get the expression for the truncated potential

$$V_T = \frac{1}{2}\omega_e^2 x^2 - \frac{\omega_e^3}{\sqrt{8D}}x^3 + \frac{7\omega_e^4}{48D}x^4. \tag{4.32}$$

We have calculated the energy of the truncated Morse oscillator by FS-MRCCM at different values of D. The comparison of the state energies calculated by FS-MRCCM, CCLRT and converged full CI is presented in table 4.1. For CCLRT calculations we used six rank of the cluster operator at ground state as well excitation operator at CCLRT. We found that these values are converged with the rank of both operators. For converged full CI calculations we used 10 harmonic oscillator basis functions. It is found that the FS-MRCC results are very close to converged full CI results. However, we found no advantage of FS-MRCC approach over CCLRT in the case of the fundamentals. This is because for the fundamentals, the CCLRT provides very accurate description due to its bi-variational nature. However, the results showed that similar accuracy in the energies can be obtained by FS-MRCCM with as low as three body excitation operator.

4.3.2 HDO Molecule

Our second case study is HDO molecule. The potential energy surface data are taken from reference [15]. The results are presented in table 4.2. The FS-MRCC values are compared with CCLRT with different rank of excitation operator and with full CI results. For full CI calculation we used 10-18-10 harmonic oscillator basis set and found that these numbers are converged with the number of basis functions. We found that the FS-MRCC results are close to the full CI results. The comparison between the FS-MRCC

Table 4.2: Energies of the fundamentals of HDO molecule:Units are in cm^{-1}.

State	CCLRT			MRCC	Full CI
	3 boson	4 boson	5 boson		
100	7154.78	7155.43	7155.52	7154.65	7155.55
010	6184.23	6182.95	6182.88	6184.43	6182.95
001	8211.15	8213.07	8212.55	8213.34	8212.22

results and the CCLRT results signifies that the FS-MRCC results are not converged with the rank of excitation operator.

4.4   Conclusion

In this work, we presented the general formulation of the Fock space multireference coupled cluster method in bosonic representation to describe the molecular anharmonic vibrations. We presented the results for the fundamental states of one dimensional truncated Morse oscillator and HDO molecule with *ab initio* potential energy surface. In these illustrative examples, we found that the vibrational energies of molecules can be obtained by the FS-MRCCM with a low rank of the excitation operator with accuracy closed to converged full CI. For the fundamental states, however, we do not find any significant advantage of FS-MRCCM over CCLRT since the CCLRT describes these states very accurately. However, since the FS-MRCC describes the shifting of the centroid of the vibrational wave functions this method is ought to provide a better description for the higher excited states.

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Chapter 5

Summaries and Future Aspects

The main goal of this thesis was to develop the coupled cluster method to study molecular anharmonic vibration. The most attractive feature of the coupled cluster method is that it provides accurate results comparable to full CI even at a approximate calculation. Motivated by the various attractive features of the bosonic representation, we explored different aspect of the coupled cluster method in this representation. In our first study, we use the coupled cluster linear response theory (CCLRT) for the excited state descriptions. A systematic study on the convergence pattern of vibrational energies is performed with respect to the rank of the both cluster operator at ground state as well as excitation operator for CCLRT. With illustrative examples of different tri-atomic and tetra-atomic molecules, our study shows that one can achieve accuracy in the excitation energies comparable with full CI by coupled cluster method in bosonic representation with a low rank of excitation operator. In terms of CPU time the performance of the CCM in this representation is extremely good.

   The hierarchical feature of the CCLRT method is that it uses an effective Hamiltonian

generated by a similimarity transformation with the exponential wave operator to calculate excitation energies. Such an effective Hamiltonian is manifestly nonhermitian. This may leads to complex eigenvalues in an approximate calculation. We have showed that the use of a second similarity transformation in the spirit of the extended coupled cluster method (ECCM) reduces the nonhermicity in an approximate manner and removes some of the complex eigenvalues.

Having studied the convergence pattern of the vibrational state energies we turned our attention to calculate the expectation values and transition matrix elements using effective operator approach based on coupled cluster method. We presented the methodology and some pilot results in the third chapter. We performed the convergence pattern of these quantities with the rank of the excitation operator in CCLRT. A detail analysis is made on the significance of the ECCM approach over the NCCM approach to calculate these quantities. It is found that the ECCM approach does not provide any significant improvement over NCCM approach as far as state energies and expectation values are concern. However, the ECCM gives a better description of the transition matrix elements due to its exponentially parametrized bra vector. In summary of the work presented in second and third chapter we can say that the coupled cluster method with CCLRT provides accurate descriptions for the lower lying vibration states of molecules.

However, the coupled cluster method with CCLRT does account for the state specific descriptions of the shifting of the centroid and scaling of wave functions which is required for the proper description of high energy states. In the fourth chapter, we formulated the Fock space multireference coupled cluster method that provides adequate description of the shifting of the centroid of the wave function.

In conclusion of the presented studies in this thesis, we can say that the coupled cluster method in bosonic representation is an attractive alternative to study the molecular anharmonic vibrational spectra accurately. It provides the full CI accuracy with much less computational cost. However, the success of the presented methodology motivates for some other future study:

145

a) The solution of the coupled nonlinear equations of the FS-MRCCM presented in the fourth chapter uses quasi-linearization technique using Jacobi algorithm. In this method the equations for the cluster amplitudes (e.g. for evaluating S^1 matrix elements) are written compactly as

$$A + BS^1 + CS^{1^2} + DS^{1^3} + ES^{1^4} = 0. \tag{5.1}$$

With a little algebraic manipulation this equation is written as

$$S^1 = B_0^{-1}[A + (B - B_0)S^1 + CS^{1^2} + DS^{1^3} + ES^{1^4}]. \tag{5.2}$$

The diagonal matrix B_0 contains the terms $\omega_i + \omega_j - \omega_k$. Hence, this method suffers from convergence problem when the resonance between vibrational modes are strong i.e. when $\omega_i + \omega_j \approx \omega_k$. As discussed before, this kind of situations are very common in molecular vibration, for example, between stretching and bending motions. Hence, the solution of the FS-MRCC equations demands a sophisticate numerical solution that can avoid this resonance problem.

b) The idea of effective operator based approach to calculate the non-energetic properties or transition matrix elements can be extended for the FS-MRCC approach. In FS-MRCC, one constructs the effective Hamiltonian via similarity transformation of the physical Hamiltonian using a valence universal wave operator,

$$H_{eff} = \Omega^{-1}H\Omega. \tag{5.3}$$

Since the H_{eff} is a similarity transformation of H, these properties can be calculated by obtaining the left and right eigenvectors of H_{eff}.

The effective Hamiltonian in Eq. 5.3 is in block triangular form by virtue of equation,

$$QH_{eff}P = 0. \tag{5.4}$$

This effective Hamiltonian is not a convenient choice for calculating the non-energetic properties or transition matrix elements since the left eigenvectors of such effective

Hamiltonian span the full Hilbert space. For such calculations it is desirable to construct H_{eff} that is block diagonal. This means, in addition of Eq. 5.4, the effective Hamiltonian should satisfy

$$PH_{eff}Q = 0. \tag{5.5}$$

Sree Latha and Prasad [1] showed that this requirement is satisfied while retaining the validity of subsystem embedding condition if the wave operator is chosen in the form of

$$\Omega = e^{S^0}e^{-\sigma^0}e^{S^1}e^{-\sigma^1}e^{S^2}e^{-\sigma^2}... \tag{5.6}$$

The effective Hamiltonian with such a wave operator takes the form,

$$H_{eff} = e^{\sigma^m}e^{-S^m}..e^{-S^1}e^{\sigma^0}e^{-S^0}He^{S^0}e^{-\sigma^0}e^{S^1}e^{-\sigma^1}...e^{S^m}e^{-\sigma^m} \tag{5.7}$$

It can be easily seen that for zero valence problem, the form of effective Hamiltonian reduces to the form defined by Arponen [2–4] in extended coupled cluster method,

$$H_{eff}^{00} = e^{\sigma^0}e^{-S^0}He^{S^0}e^{-\sigma^0}. \tag{5.8}$$

The cluster matrix elements S^0 are determined from

$$Q^0e^{-S^0}He^{S^0}P^0 = Q^0H^1P^0 = 0. \tag{5.9}$$

Once the S^0 matrix elements are determined, the σ^0 are obtained from the equation

$$P^0e^{\sigma}H^1e^{-\sigma}Q^0 = P^0H^{1'}Q^0 = 0. \tag{5.10}$$

Similarly, S^1 matrix elements for one valence sectors are determined from

$$P^1e^{-S^1}H^{1'}e^{S^1}Q^1 = P^1H^2Q^1 = 0, \tag{5.11}$$

and subsequently, the σ^1 matrix elements are obtained from the condition

$$Q^1e^{\sigma^1}H^2e^{-\sigma^1}P^1 = 0. \tag{5.12}$$

This process can be continued till the effective Hamiltonian is completely block diagonal. For the final block diagonal effective Hamiltonian, the eigenvectors are confined to

the model space. Extending the idea of effective operator approach described in the third chapter, one can calculate the expectation values of any operator O with these eigenvectors and the effective operator defined as

$$O_{eff} = \Omega^{-1}O\Omega. \tag{5.13}$$

c) It is well known that the rotational degrees of freedoms are strongly coupled with the vibrational motions. In the presented work of the thesis we used the Watson Hamiltonian [5] in the normal coordinate which decouples the rotational and vibrational degrees of freedom in most convenient manner

$$\hat{H} = \sum_{\alpha,\beta} \frac{1}{2}\hbar(\hat{J}_\alpha - \hat{\pi}_\alpha)\mu_{\alpha\beta}(\hat{J}_\beta - \hat{\pi}_\beta) + \frac{1}{2}\sum_i \hat{P}_i^2 + V(Q) + U. \tag{5.14}$$

In this thesis we considered only the case of non-rotating molecules (i.e. only for J=0 in Eq. 5.14). However, it is desirable to include the rotational contributions to the molecular vibrational spectra to get the accurate description. For $J > 0$ rotational states, the contributions from the component of vibrational angular momentum (π_α) can be easily calculated by the coupled cluster approach in bosonic representation since such terms is written in terms of Coriolis coupling terms, normal coordinate (Q_i) and their conjugate momenta (Eq. 1.21). However, treatment of the total angular momentum operator is not straight forward. A linear molecule is having two rotational degrees of freedom; one is the total angular momentum and the other one is the z-component of the angular momentum in body fixed coordinate. The corresponding operator are denoted by J^2 and J_z and the corresponding eigenstates $|JM\rangle$ are associated Legendre polynomials. Here, J is the total angular- momentum quantum number and M is its projection on the body fixed Z axis. For non-linear molecules, there are three rotational degrees of freedom; the total angular momentum (J), the Z-component on the body fixed axis (K) and z-component on the space fixed axis (M).

The angular momentum operator can be represented by bosons. The general idea of representing many fermion problem by boson operator is well studied in nuclear many

body physics [6–12] . For example, let us consider, the algebra of angular momentum operator $J_\pm = J_x \pm iJ_y$ and J_z, which obey the commutation relations

$$[J_+, J_-] = J_z, [J_z, J_+] = J_+. \qquad (5.15)$$

The corresponding Hilbert space is spanned by the eigenvectors $|JM\rangle$ of J^2 and J_z operators. This Hilbert space is now mapped onto a space of bosons defined by a vacuum $|0\rangle$ and boson operators B, B^+. The boson operators satisfy the commutation relations

$$[B, B^+] = 1, B|0\rangle = 0. \qquad (5.16)$$

There are several ways possible to carry out this mapping. For example, the Holstein Primakoff representation [7–9] , the Dyson representation [10, 11], the Schwinger representation [12] etc. With the boson representation of the angular momentum operators one can persue the coupled cluster method in similar way of vibrational degrees of freedom. That is optimizing a product function associated with the rotational degrees of freedom to get the vacuum and the bosonic operators B and B^+ to construct the rest of the elements of the Fock space required for the coupled cluster formalism.

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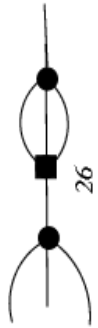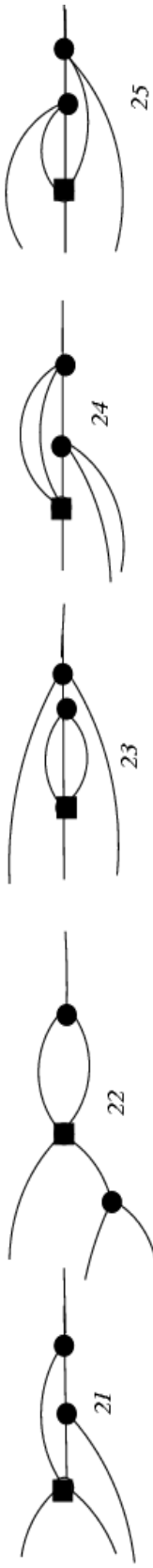
Appendix A

The Diagrammatics
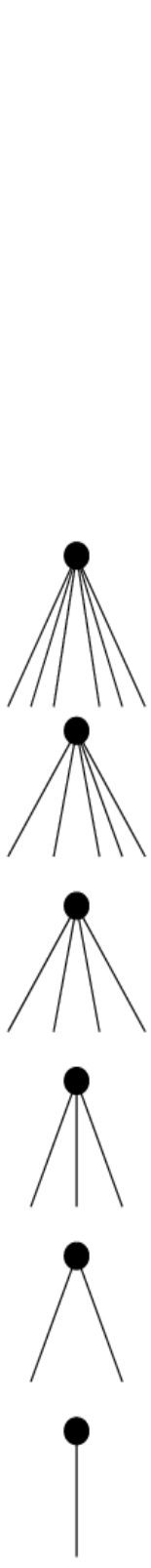
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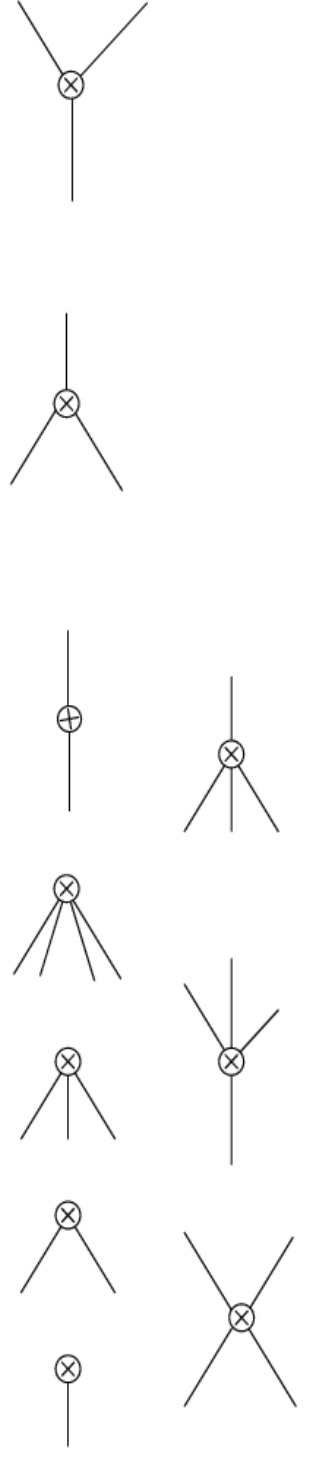
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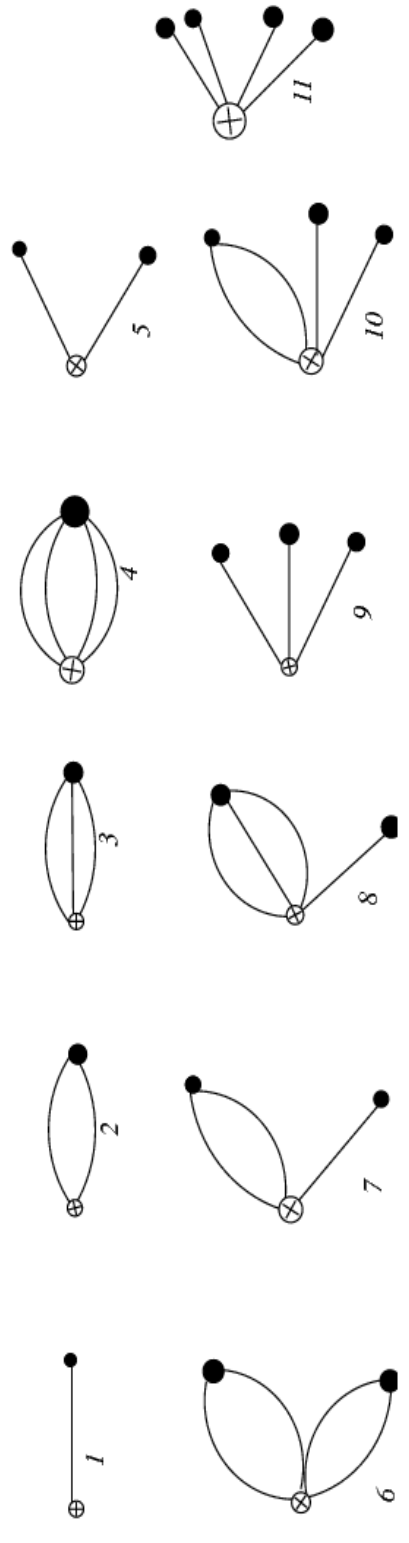
Linear Diagrams

Quadratic Diagrams

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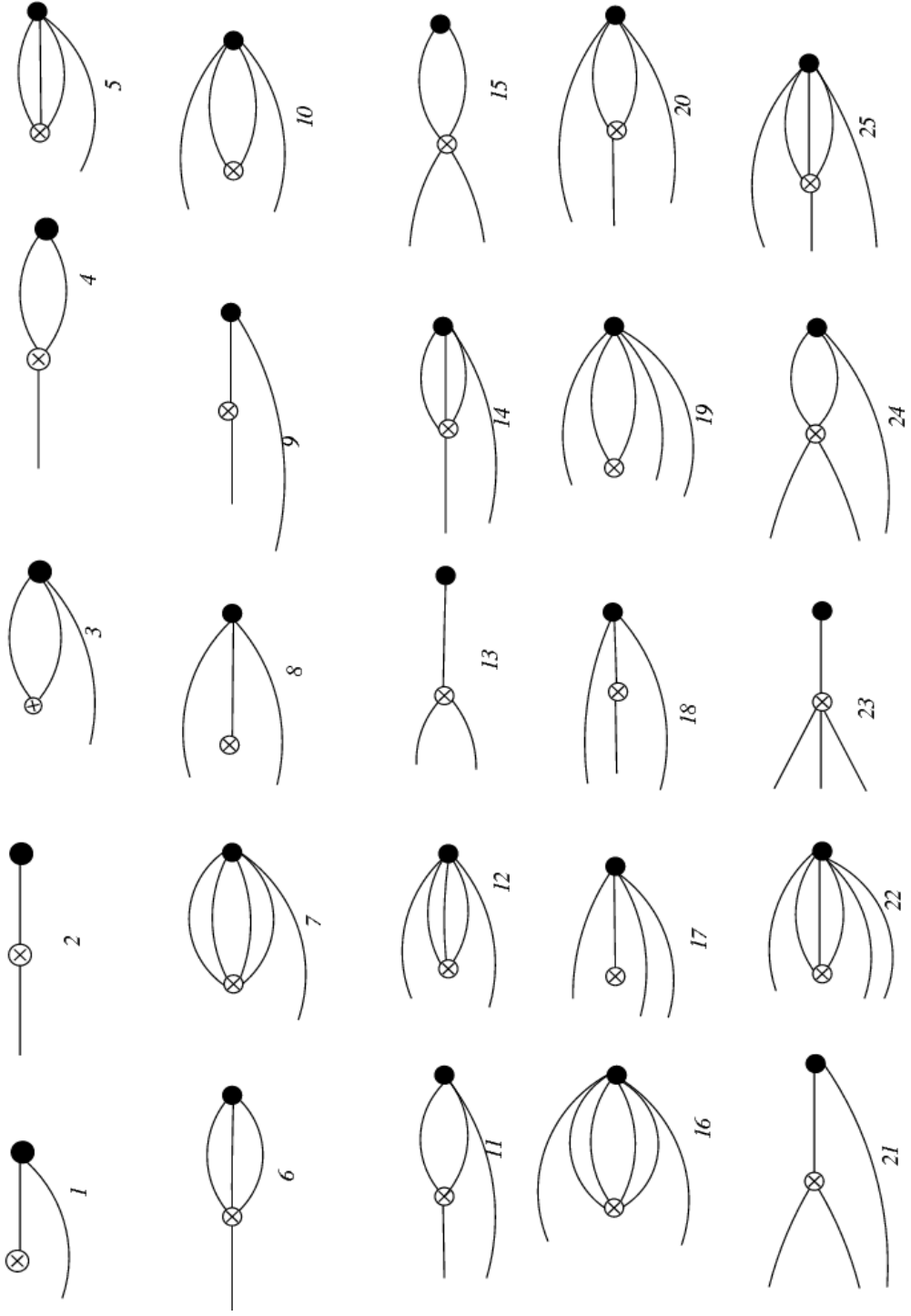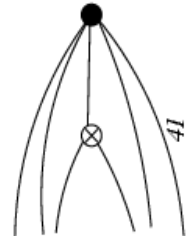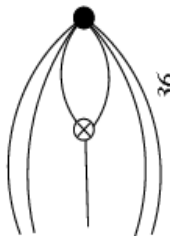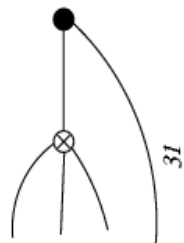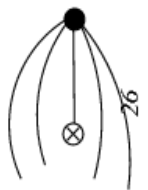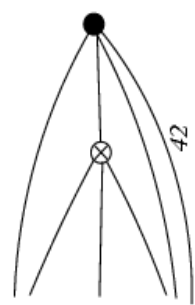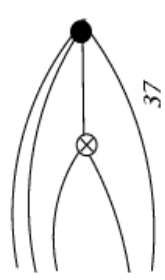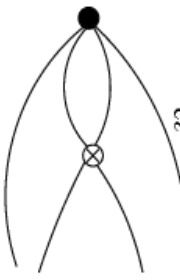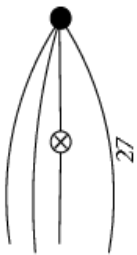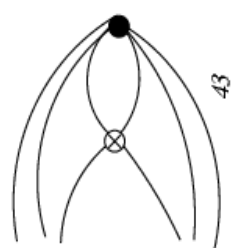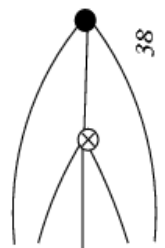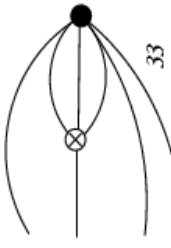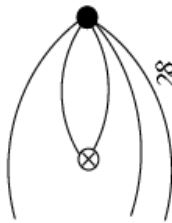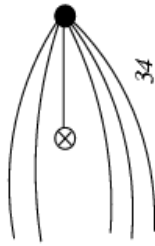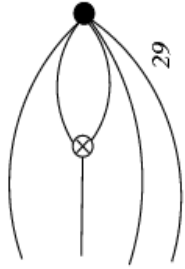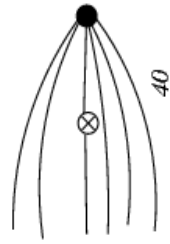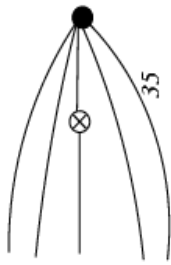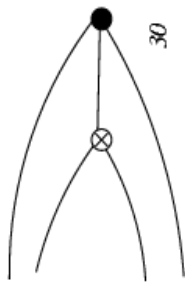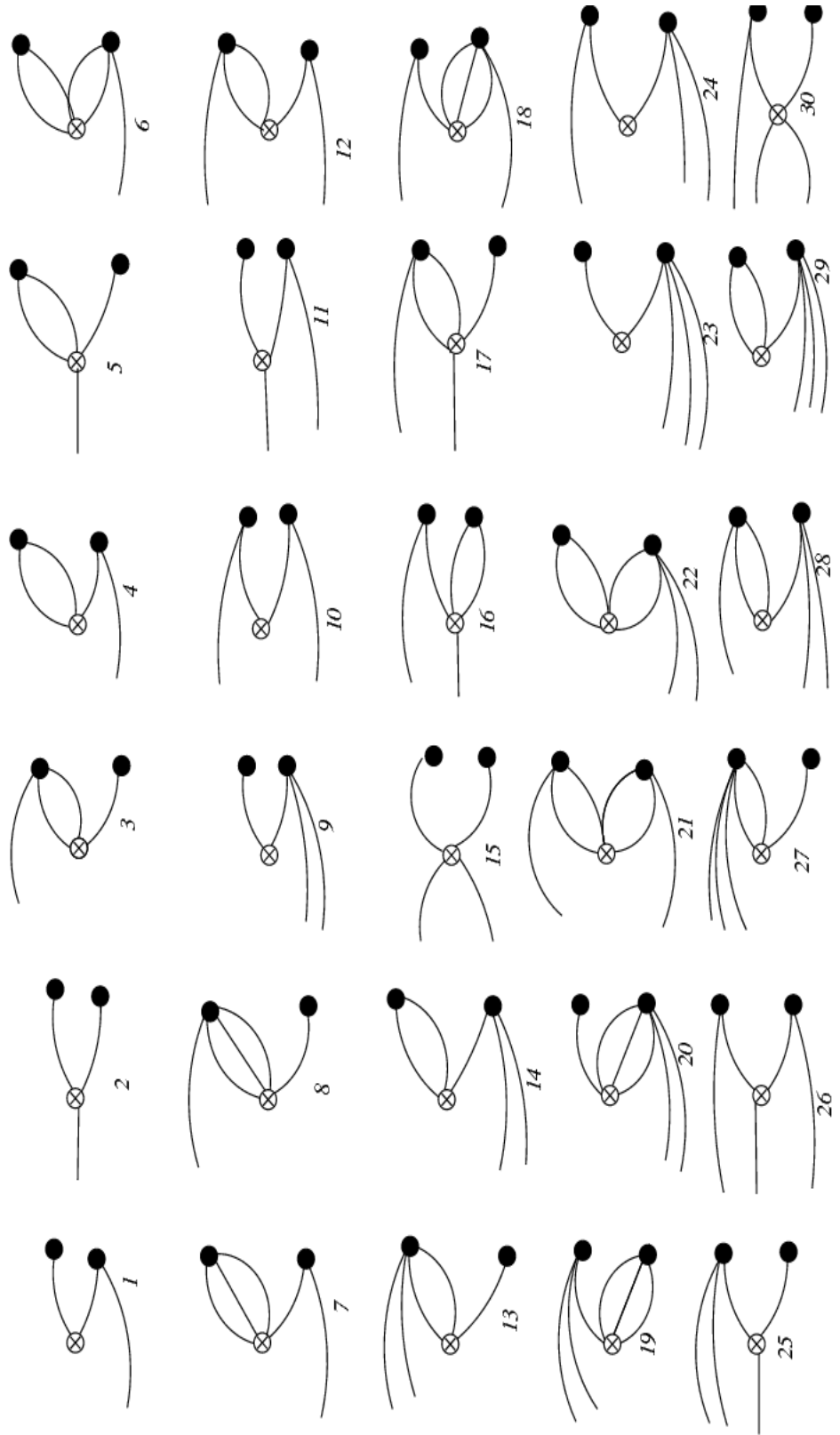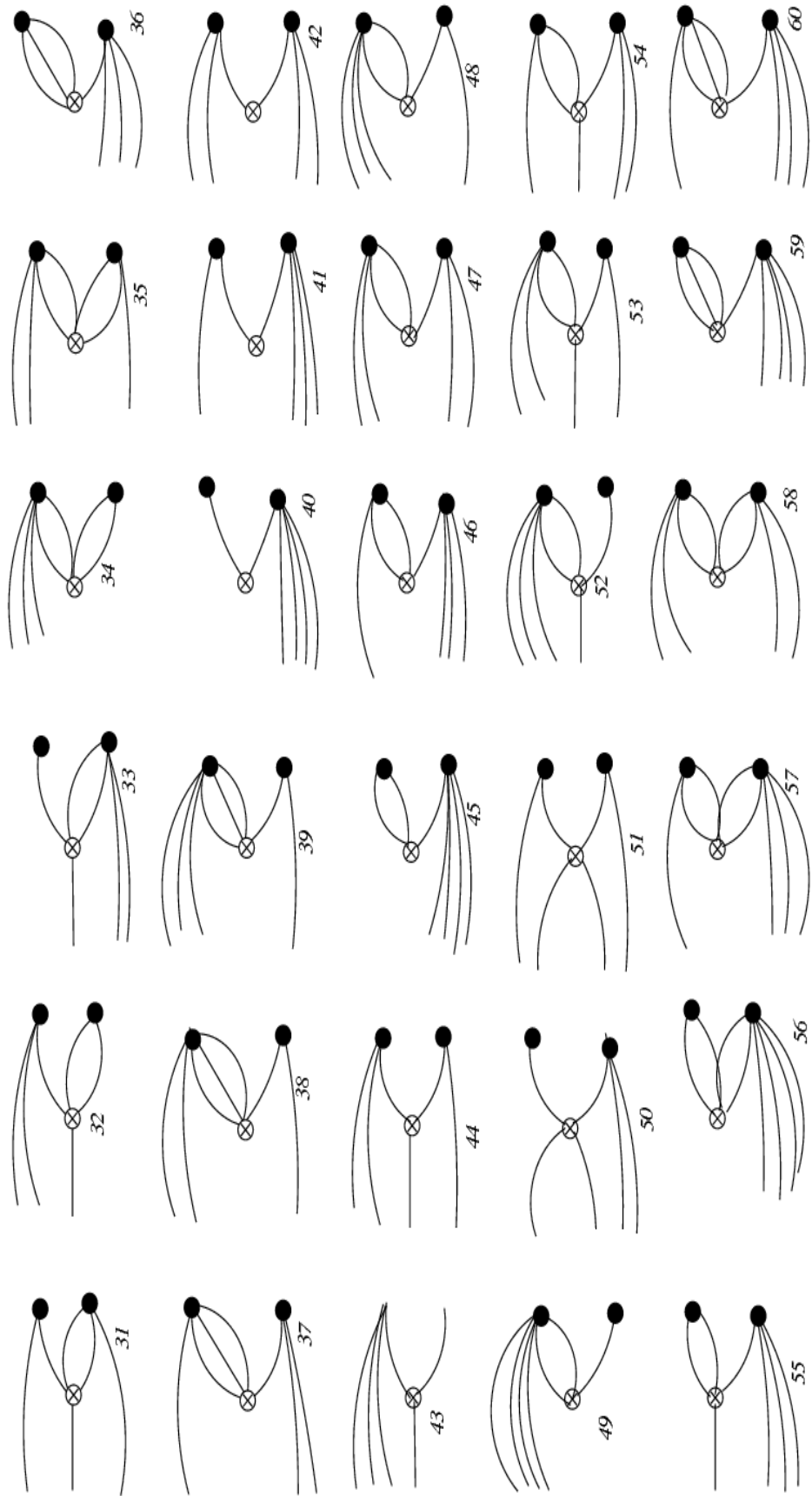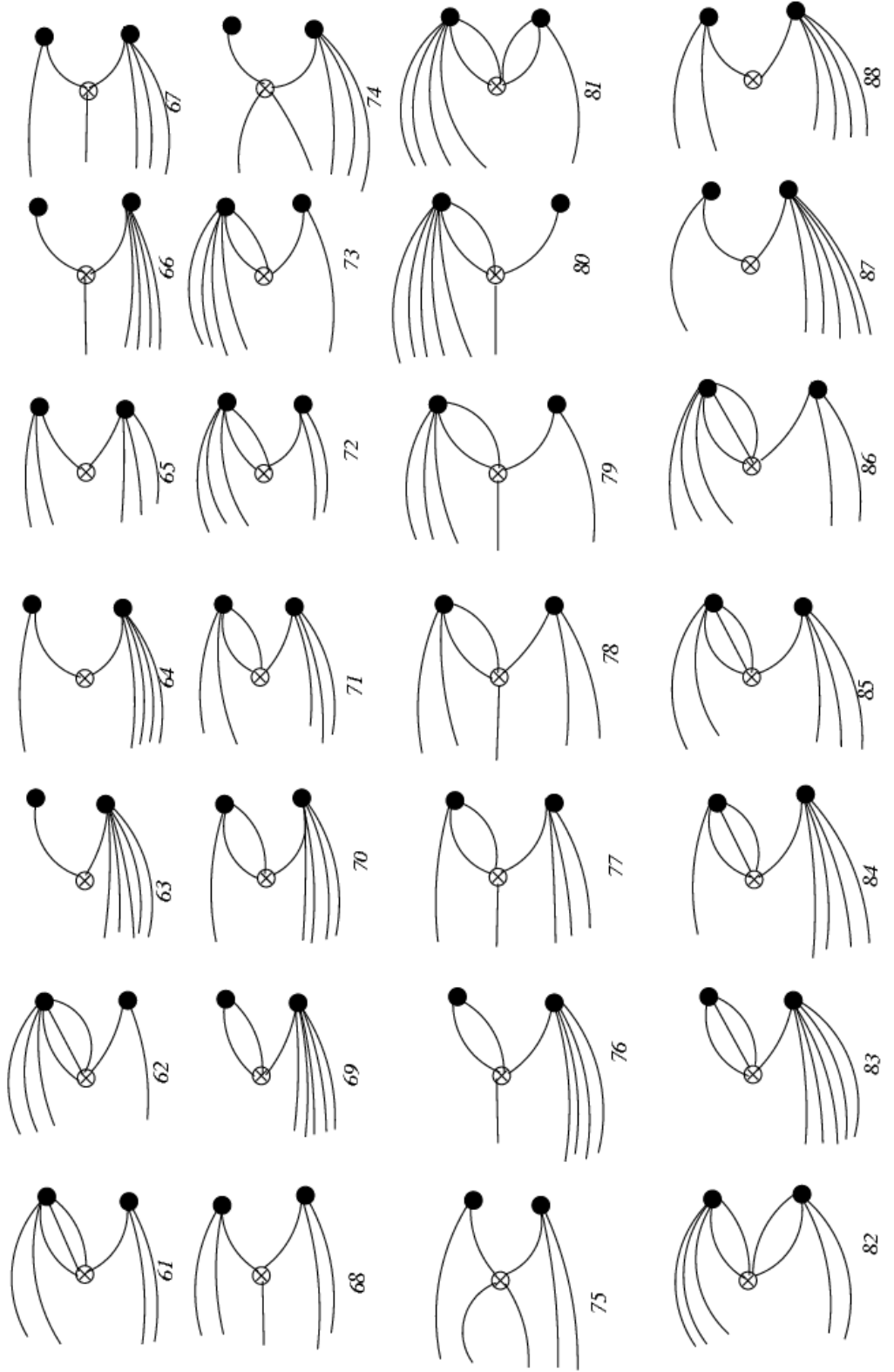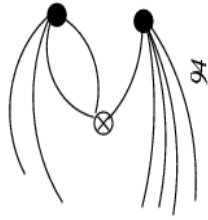
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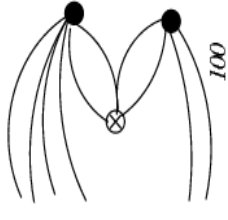
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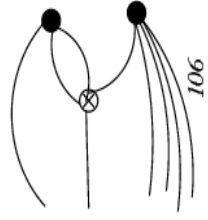
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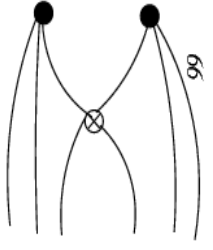
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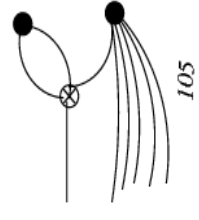
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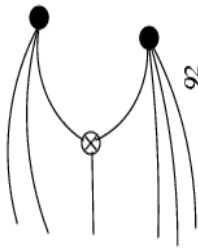
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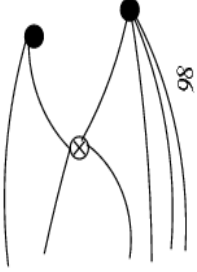
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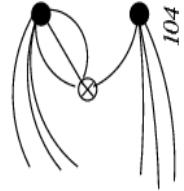
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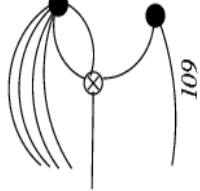
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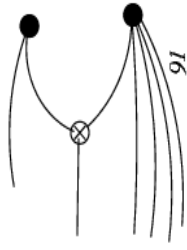
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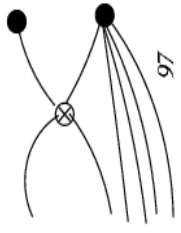
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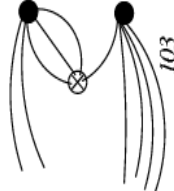
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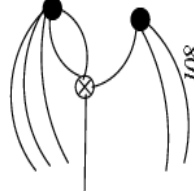
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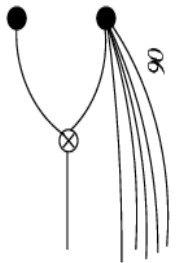
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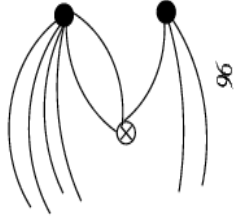
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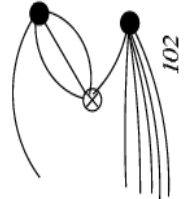
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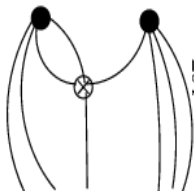
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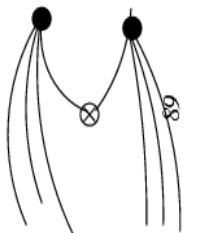
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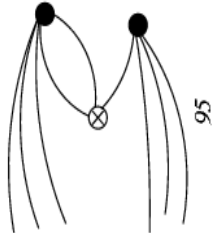
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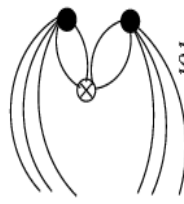
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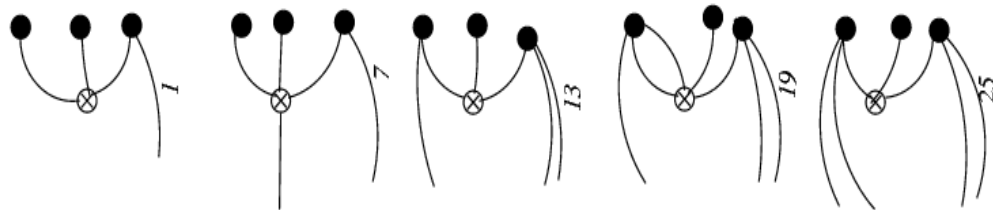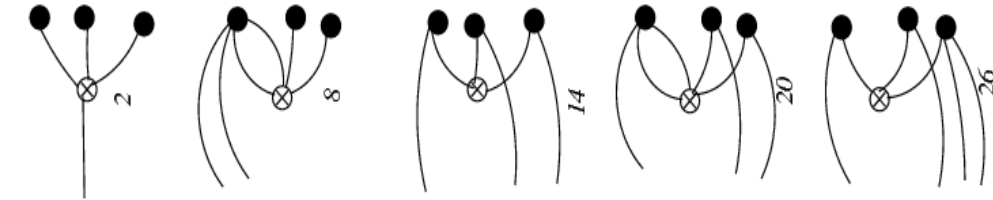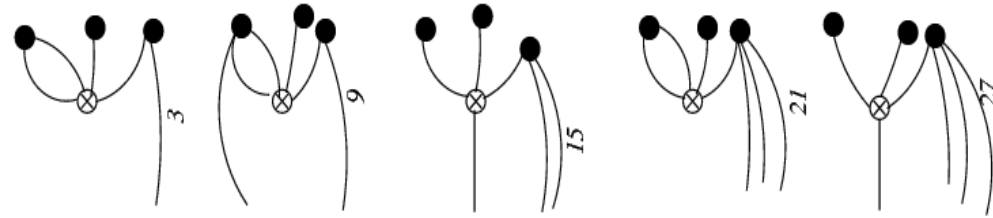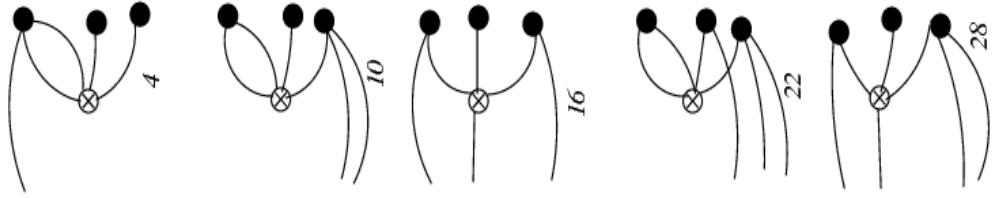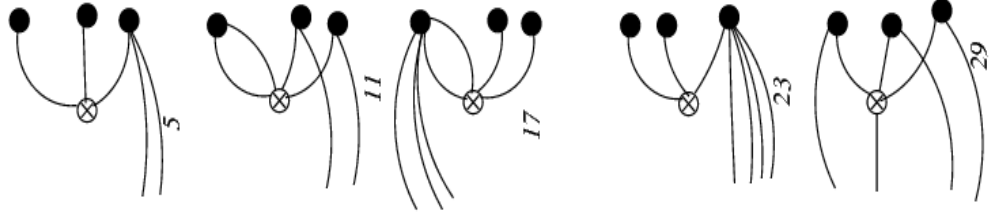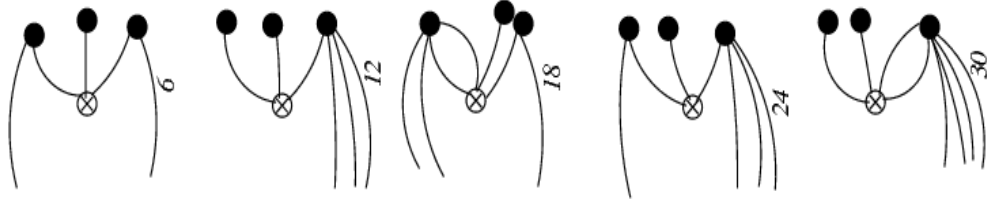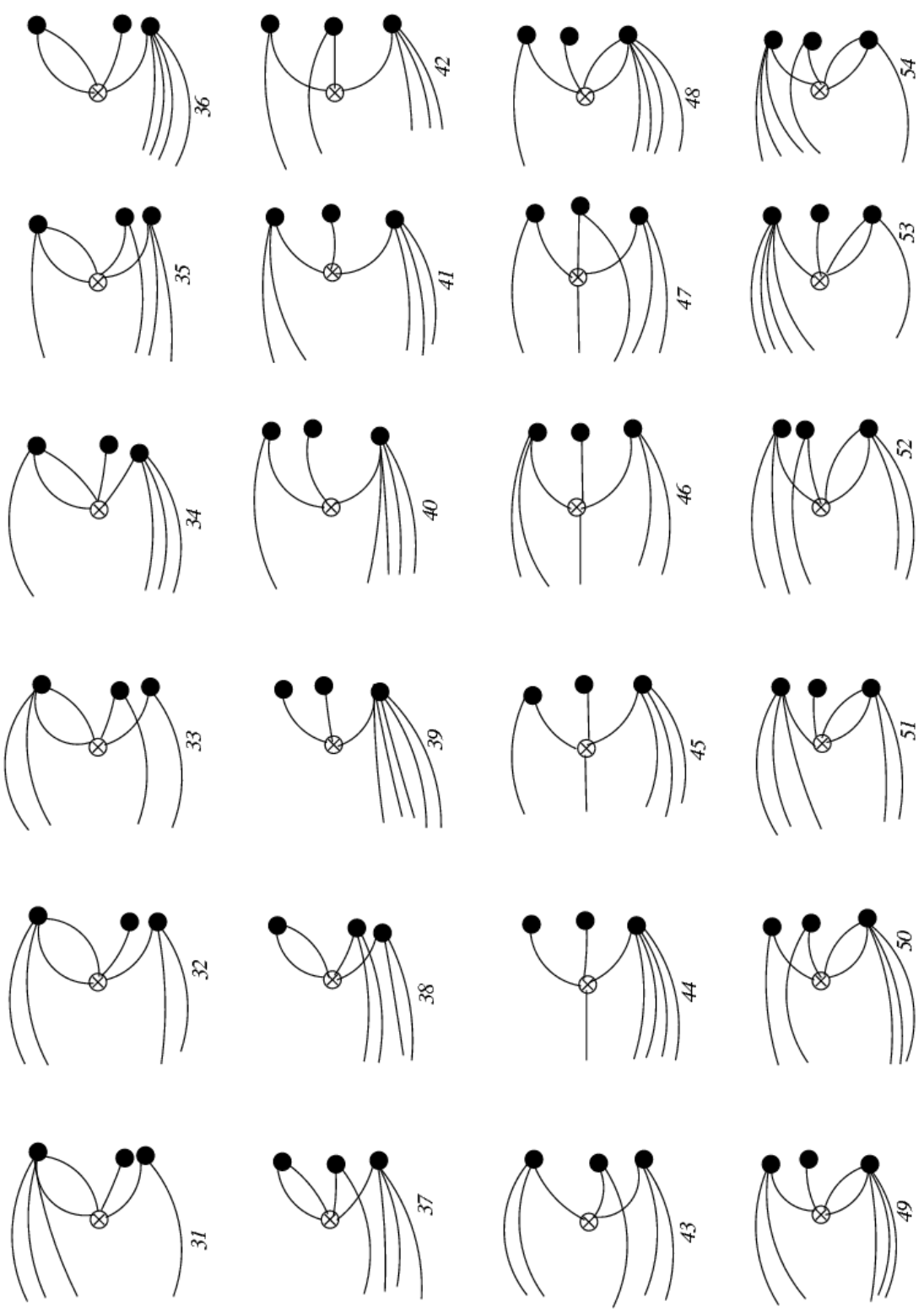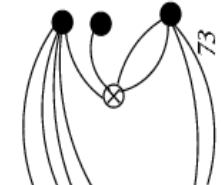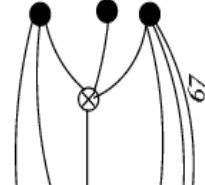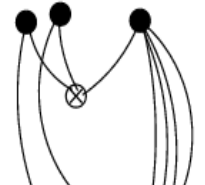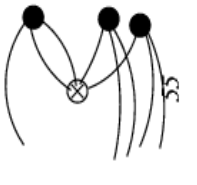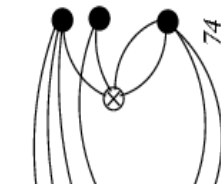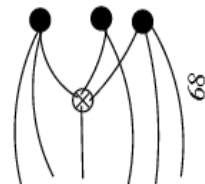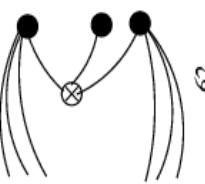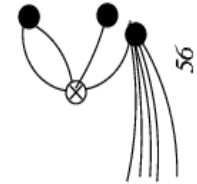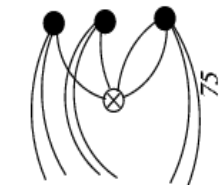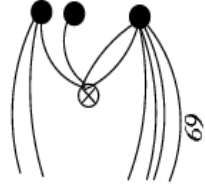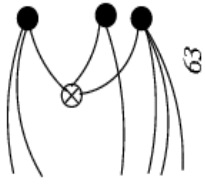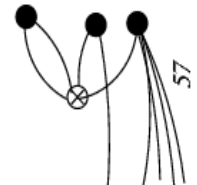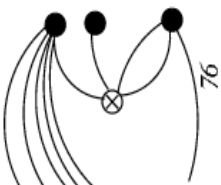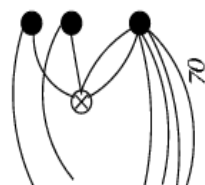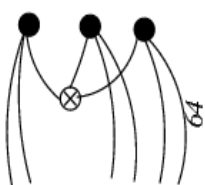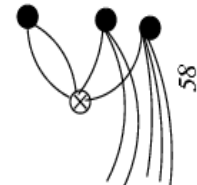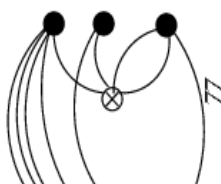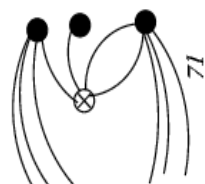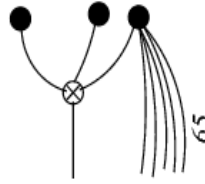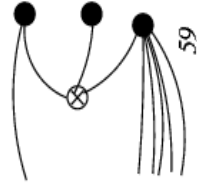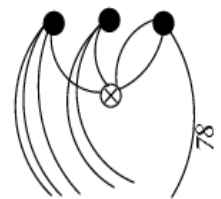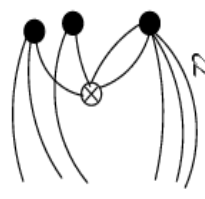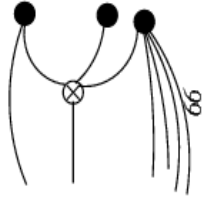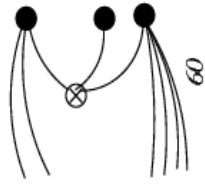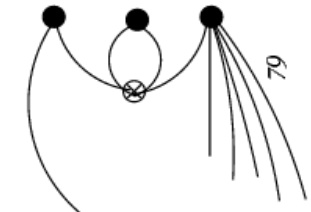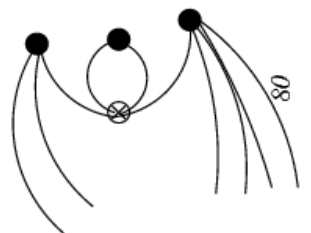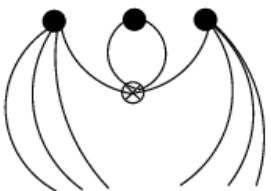
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55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78

Quartic Diagrams

Arponen Diagrams

Diagrams are generated by inverting lines of NCCM diagrams

$\sigma^{-S} \longrightarrow \blacksquare$
$e^{-S} He^{S} \longrightarrow \bullet$

Linear Diagrams

P.D. 2

PD 4

PD 6

PD 9

PD 11

PD 13

PD 14

PD 15

PD 18

PD 20

PD 21

PD 23

PD 24

PD 25

PD 27

PD 29

PD 30

PD 31

PD 32

PD 33

PD 35

PD 36

PD 37

PD 38

PD 39

PD 40

PD 41

PD 42

PD 43

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52–57 extra diagrams with VC4
58–59 Extra diagrams with VC5

60–63 extra diagrams with VC3

50 51 52 53 54 55 56
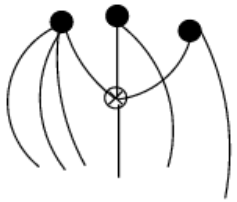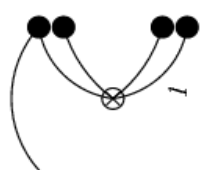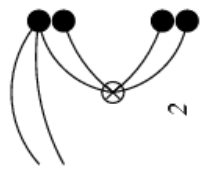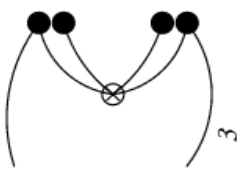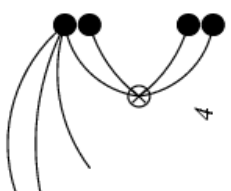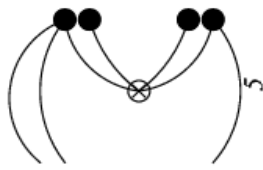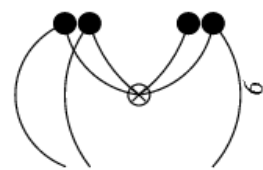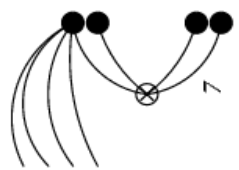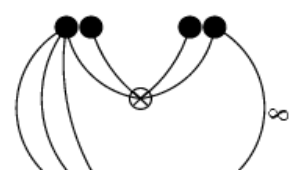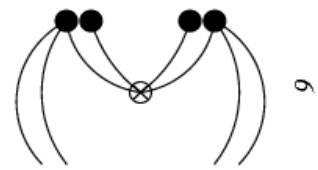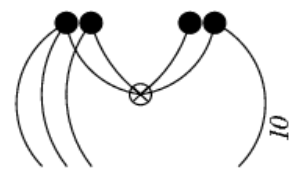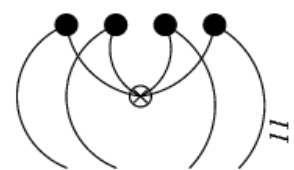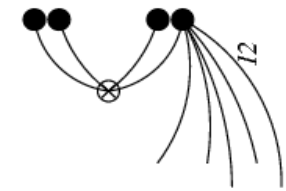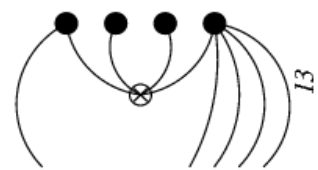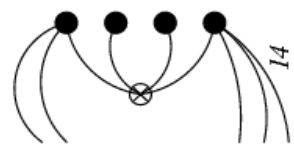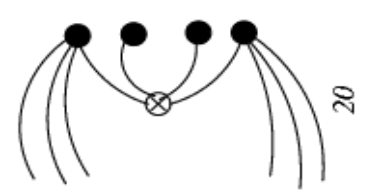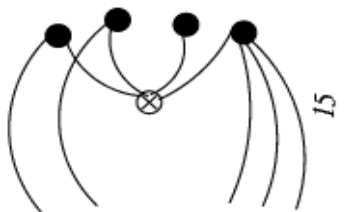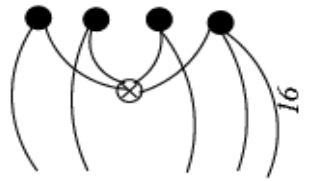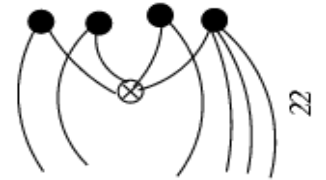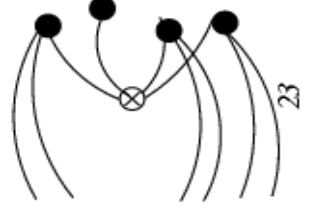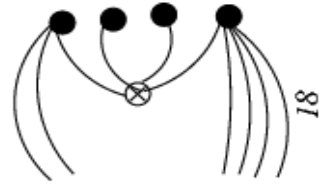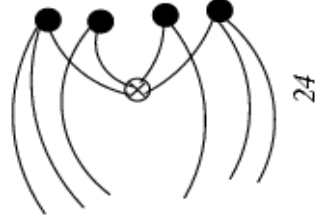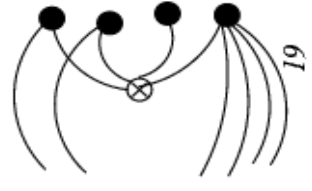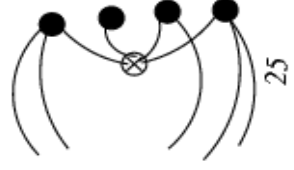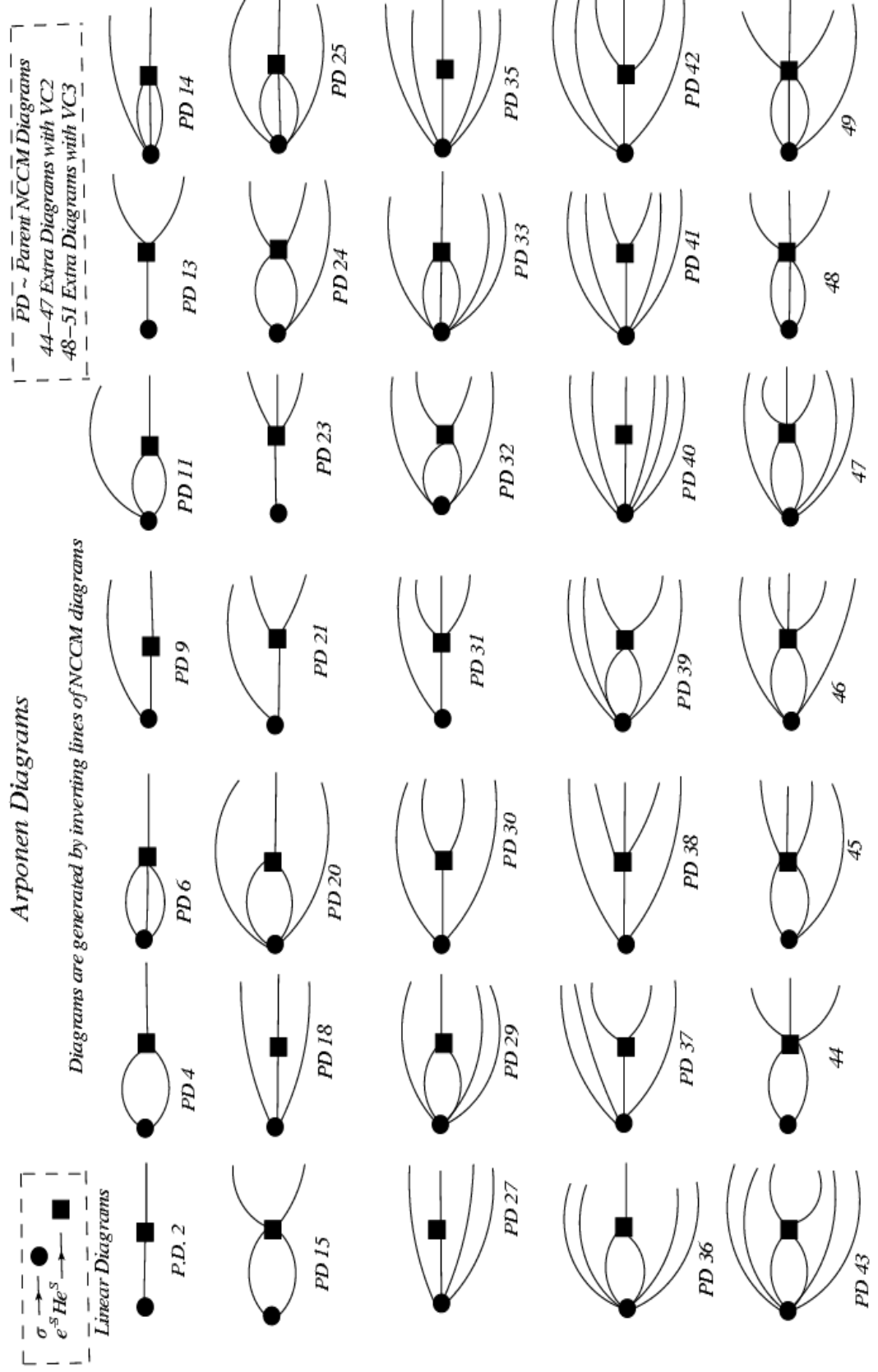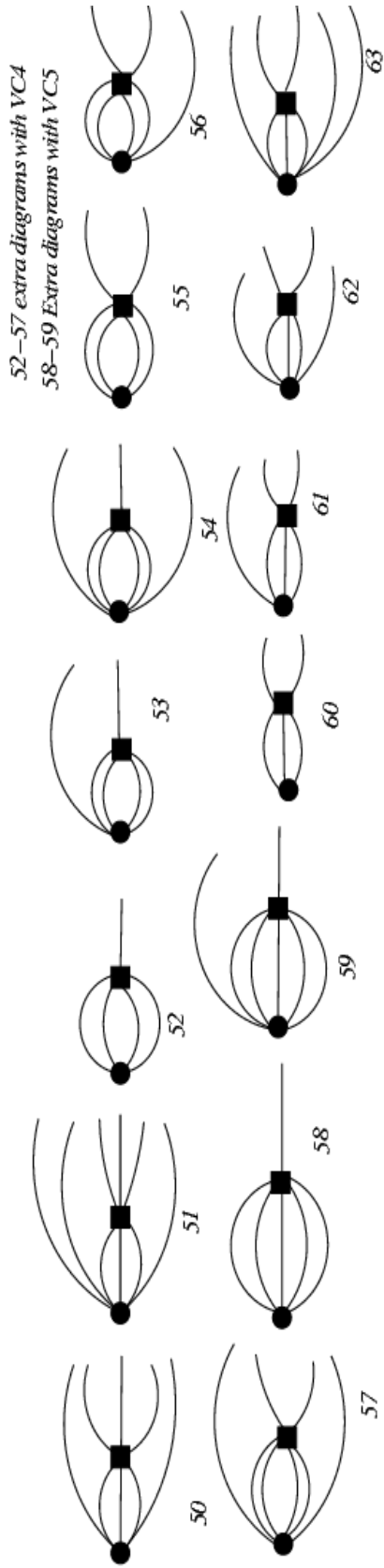
57 58 59 60 61 62 63

Quadratic Diagrams

The numbering is according to the program BOSON3

Set 1:   PD 1   PD11   PD 25   PD 43   PD 66   PD 90

Set 2   PD 5   PD 16   PD 32   PD 55   PD 76   PD 105

PD ~ Parent Diagrams

Set 4 — PD 15

Set 5 (PD 17, 31, 54, 77) — PD 17, PD 31, PD 54, PD 77

Set 6 — PD 26

Set 7 (PD 30, 50, 74, 97) — PD 30, PD 50, PD 74, PD 97

Set 8 (PD 33, 53, 78) — PD 33, PD 53, PD 78

Set 9 (PD 44, 67, 91) — PD 44, PD 67, PD 91

Set 10 — PD 51

Set 11 (PD 52, 80) — PD 52, PD 80

Set 14 (PD 79, 109)

PD 109

PD 108

PD 79

PD 107

Set 12

PD68

PD 92

Set 13 (PD 75, 98)

PD 98

PD 106

PD 75

PD 99
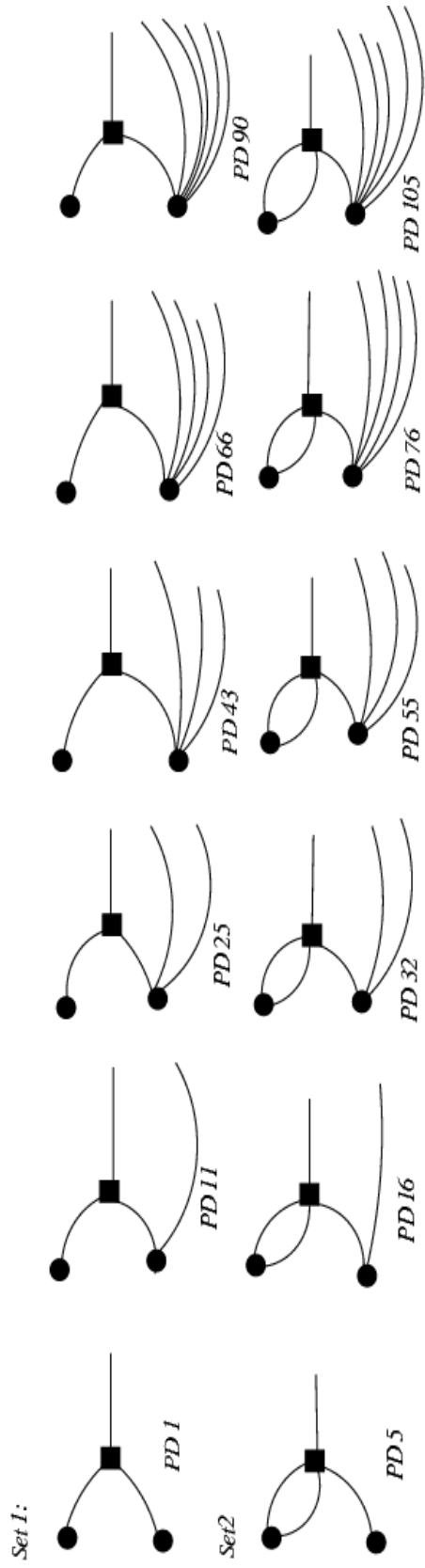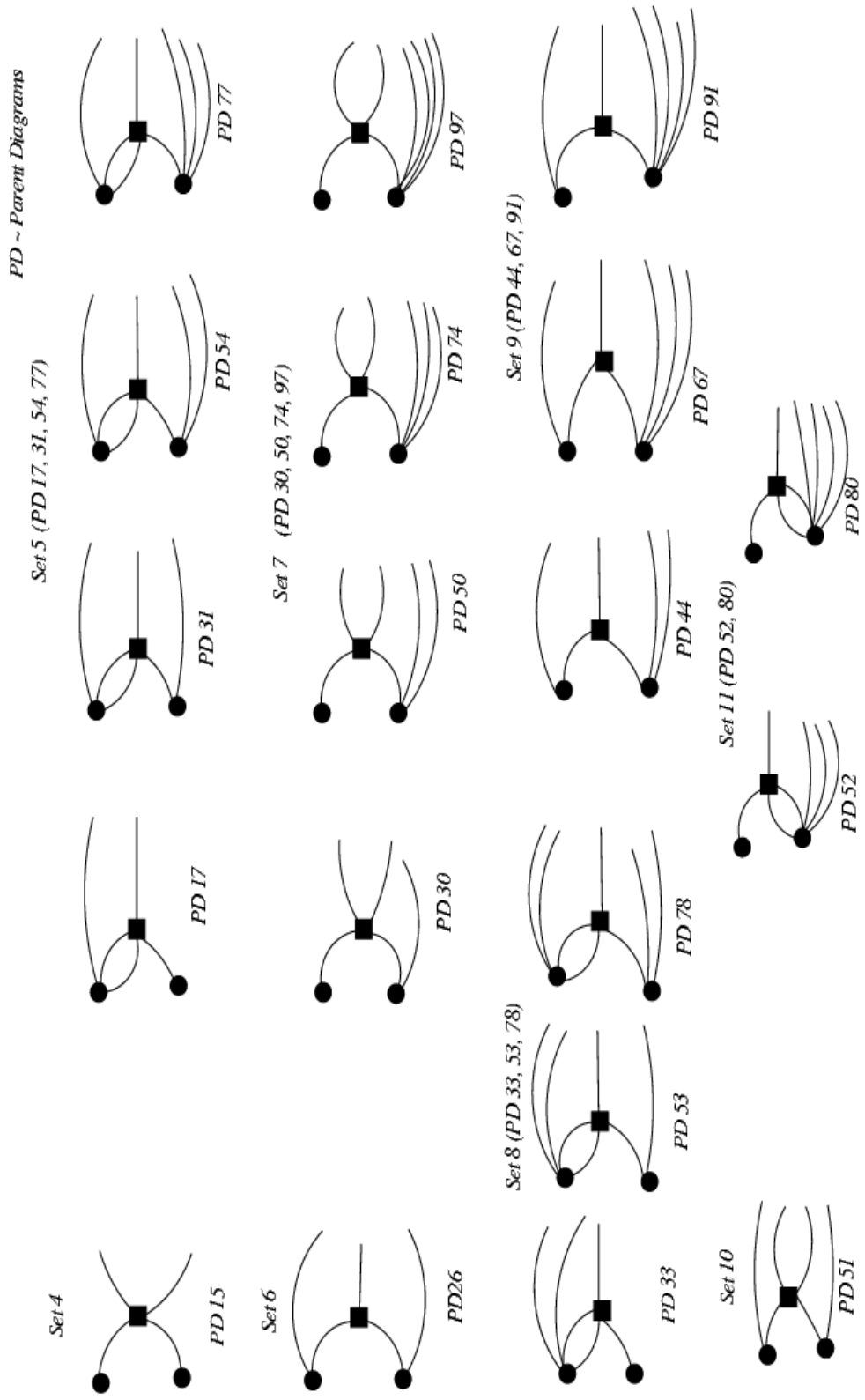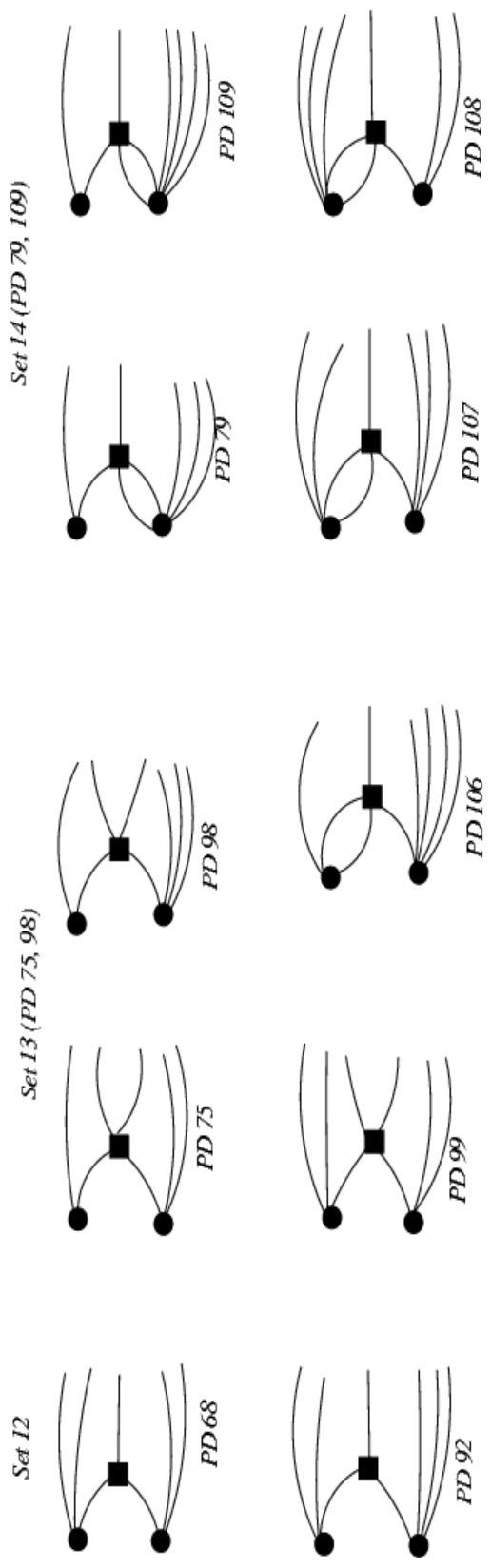
Extra Diagrams with VC2 and VC3
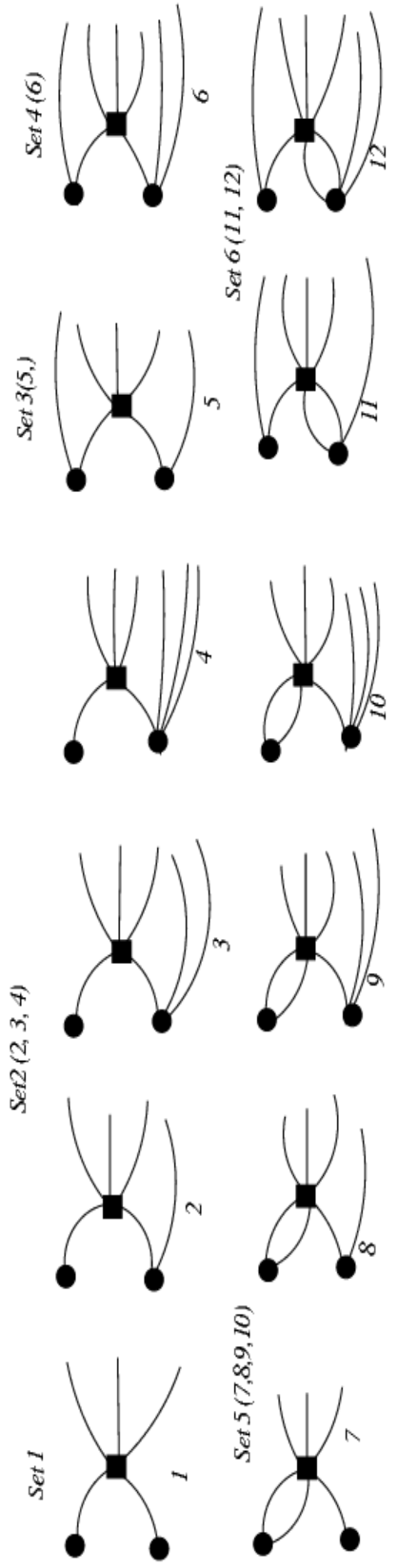
Set 1

1

Set2 (2, 3, 4)

2

3

4

Set 5 (7,8,9,10)

7

8

9

10

Set 3(5,)

5

Set 4 (6)

6

Set 6 (11, 12)

11

12

Diagrams with VC4

Set 8 (16, 17, 18, 19, 20, 21)

18

17

16

Set 10 (23, 24, 25, 26, 27)

24

23

Set 9 (22)

22

30

29

28

Set 11 (28, 29, 30, 31)

36

35

34

Set 12 (32, 33, 34, 35, 36)

33

32

31

Set 7 (13, 14, 15)

15

14

13

21

20

19

27

26

25

Set 13 (37)

Set 14 (38, 39, 40, 41)

Set 15 (42)

Set 16 (43, 44, 45, 46)

Set 17 (47, 48, 49, 50)

Set 18 (51, 52, 53)

Set 19 (54, 55, 56)

Set 20 (57, 58, 59)

Set 21 (60)

37 38 39 40 41 42

43 44 45 46 47 48

49 50 51 52 53 54

55 56 57 58 59 60

Set 19 (61)

Set 20 (62)

Set 21 (63, 64)

Set 22 (65)

Set 23 (66)

61

62

63

64

65

66

Set 24 (67)

Diagrams with VC5

67

68

69

70

72

73
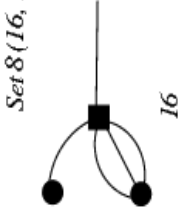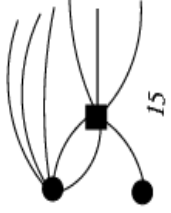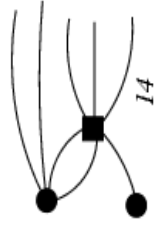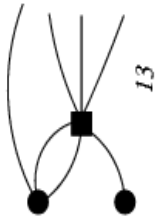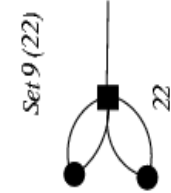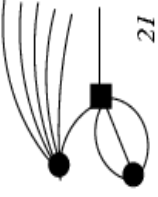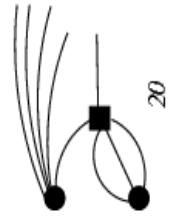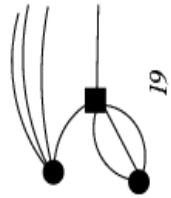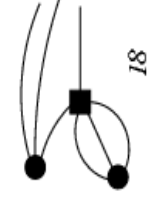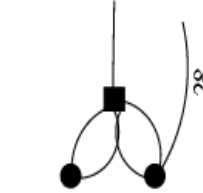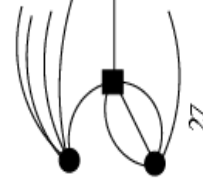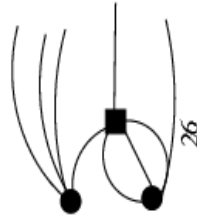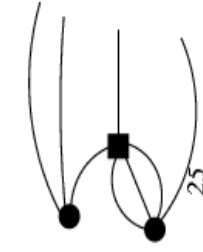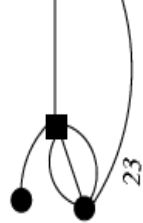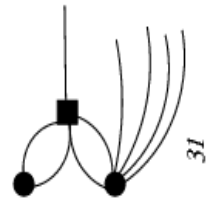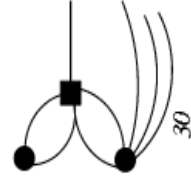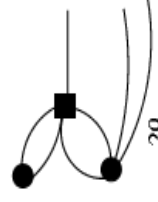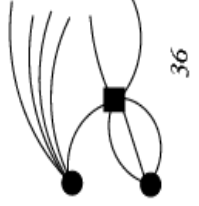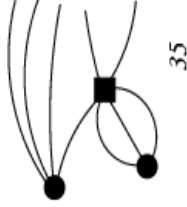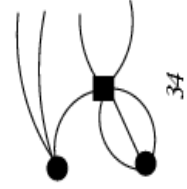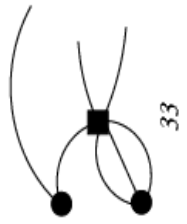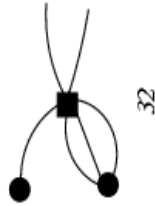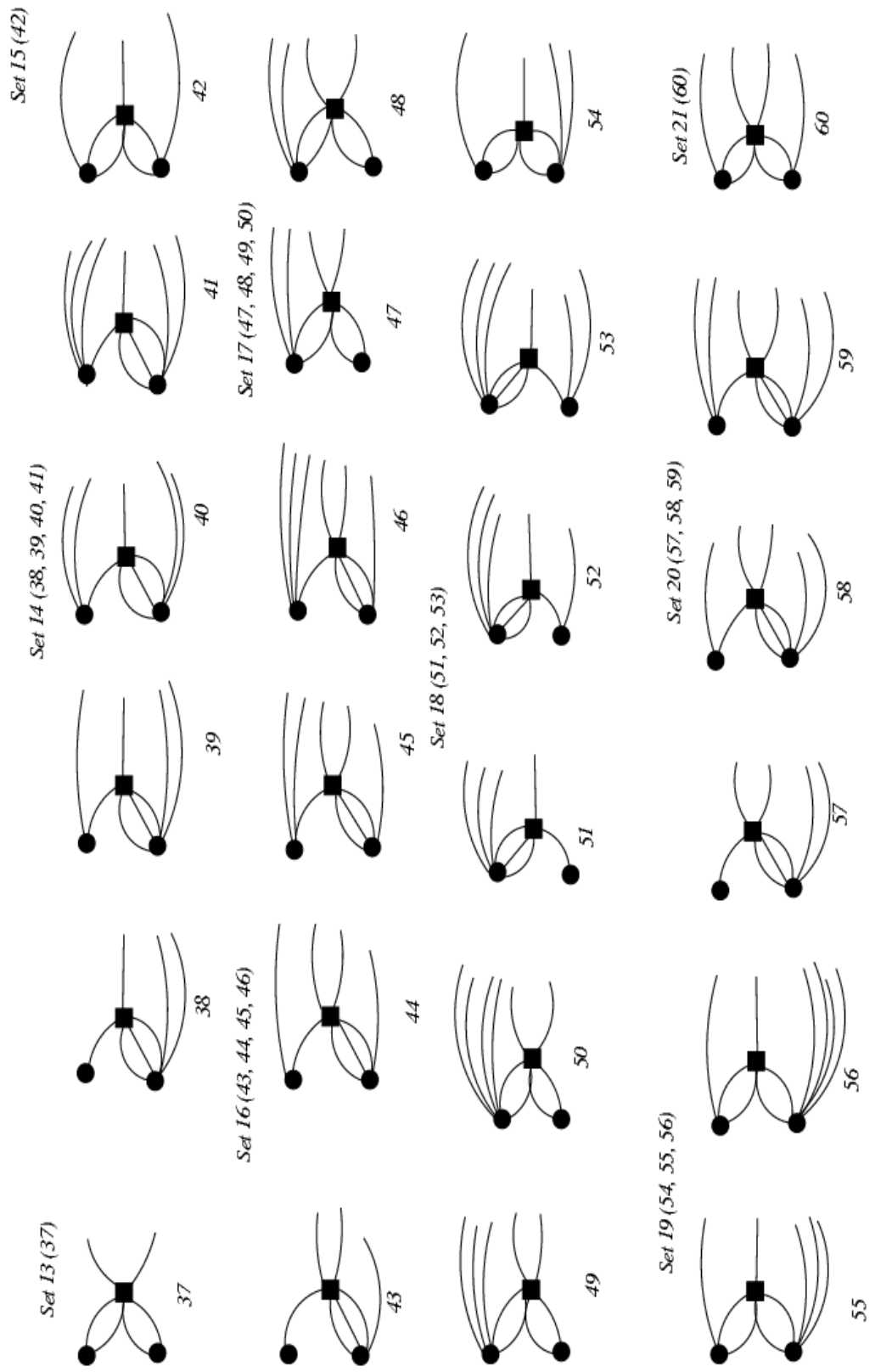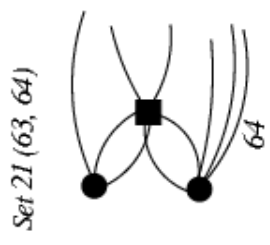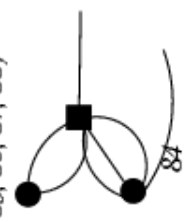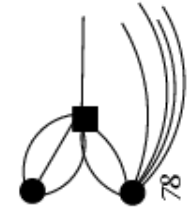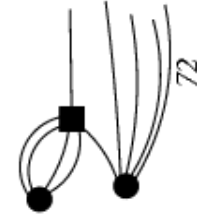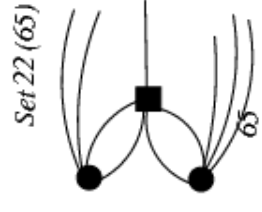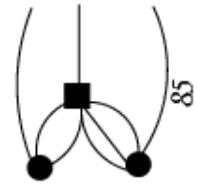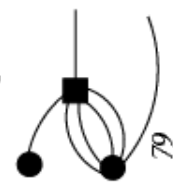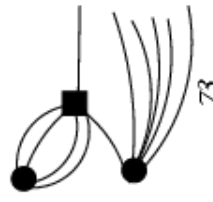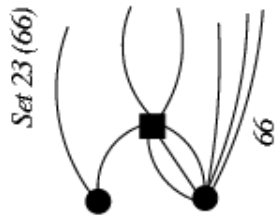
Set 25 (68, 69, 70, 71, 72, 73)

Set 26 (74, 75, 76, 77, 78)

74

75

76

77

78

Set 28 (84, 85, 86, 87, 88)

Set 27 (79, 80, 81, 82, 83)

79

80

81

82

83

84

85

104 105 106 107 108 109 110

111 112 113 114 115 116 117

118 119 120 121 122 123 124 125

126 127 128 129 130 131 132 133

134 135
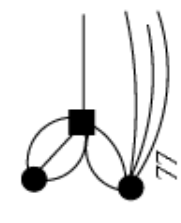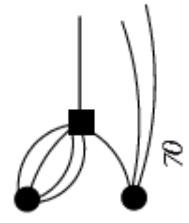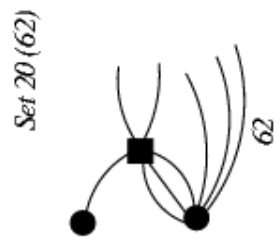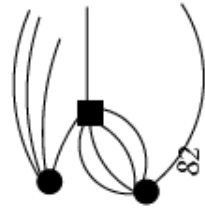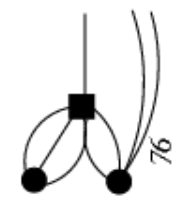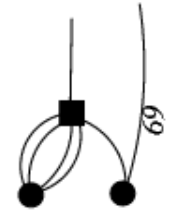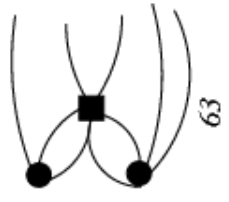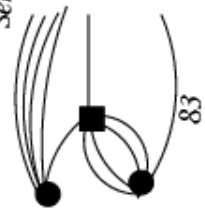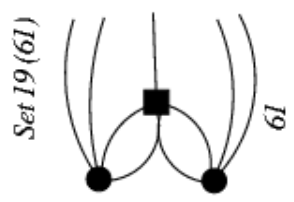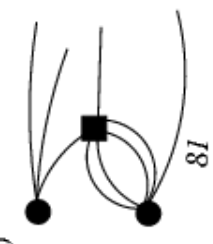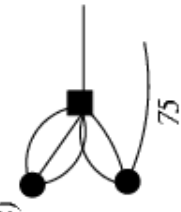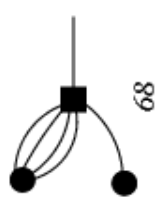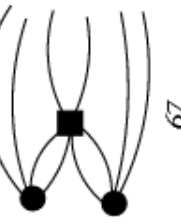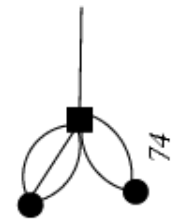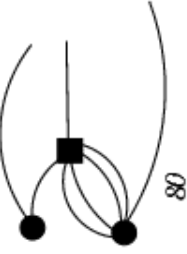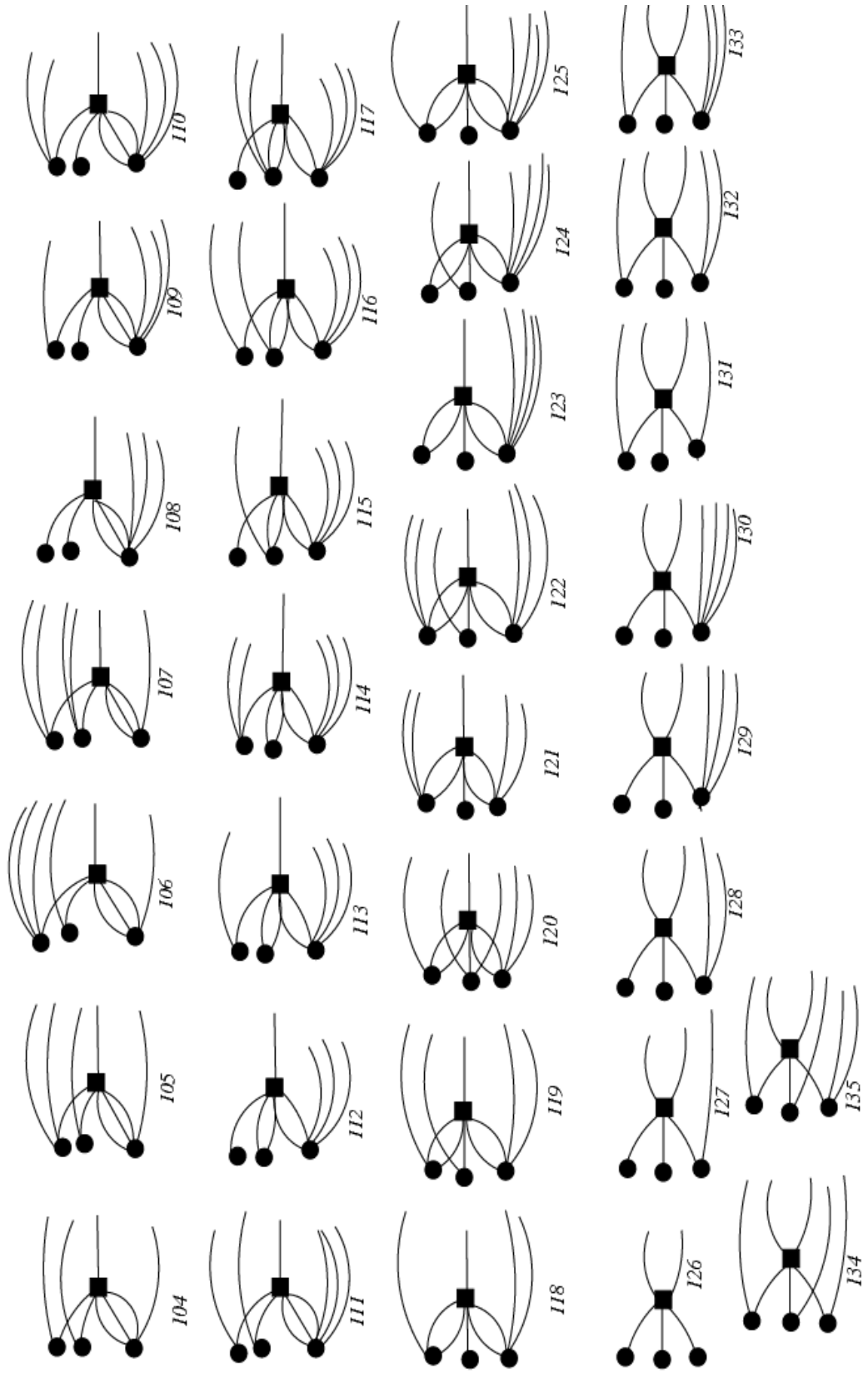
Cubic Diagrams

Set 1 (PD 2, 7, 15, 27, 44, 65)

PD 2   PD 7   PD 15   PD 27   PD 44   PD 65

Set 2 (PD 16, 46, 67)

PD 16   PD 46   PD 67   PD 28   PD 45   PD 66
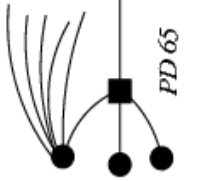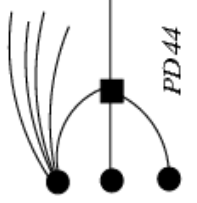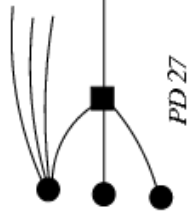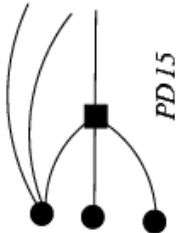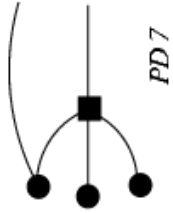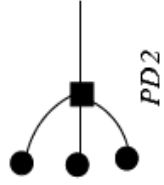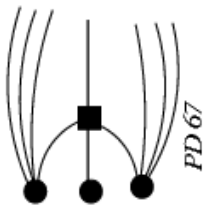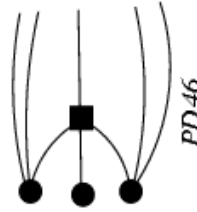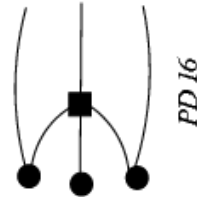
Set 3 (PD 28, 45, 66)

Set 4

PD 29   PD 47   PD 82   PD 68
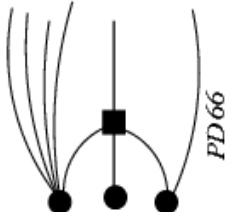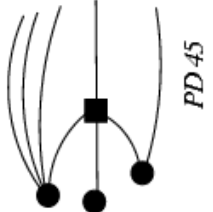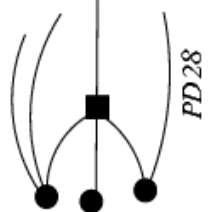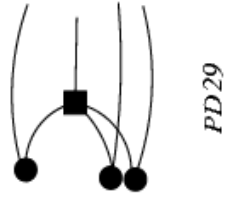
Set 5 (PD 47, 82)
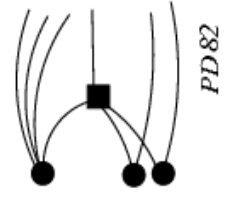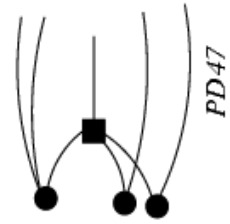
Set 6
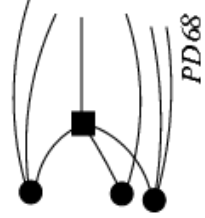
Extra Diagrams with VC3, VC4 and VC5

82 81 80 79 78 77 76

89 88 87 86 85 84 83

96 95 94 93 92 91 90

103 102 101 100 99 98 97

104 105 106 107 108 109 110
111 112 113 114 115 116 117
118 119 120 121 122 123 124 125
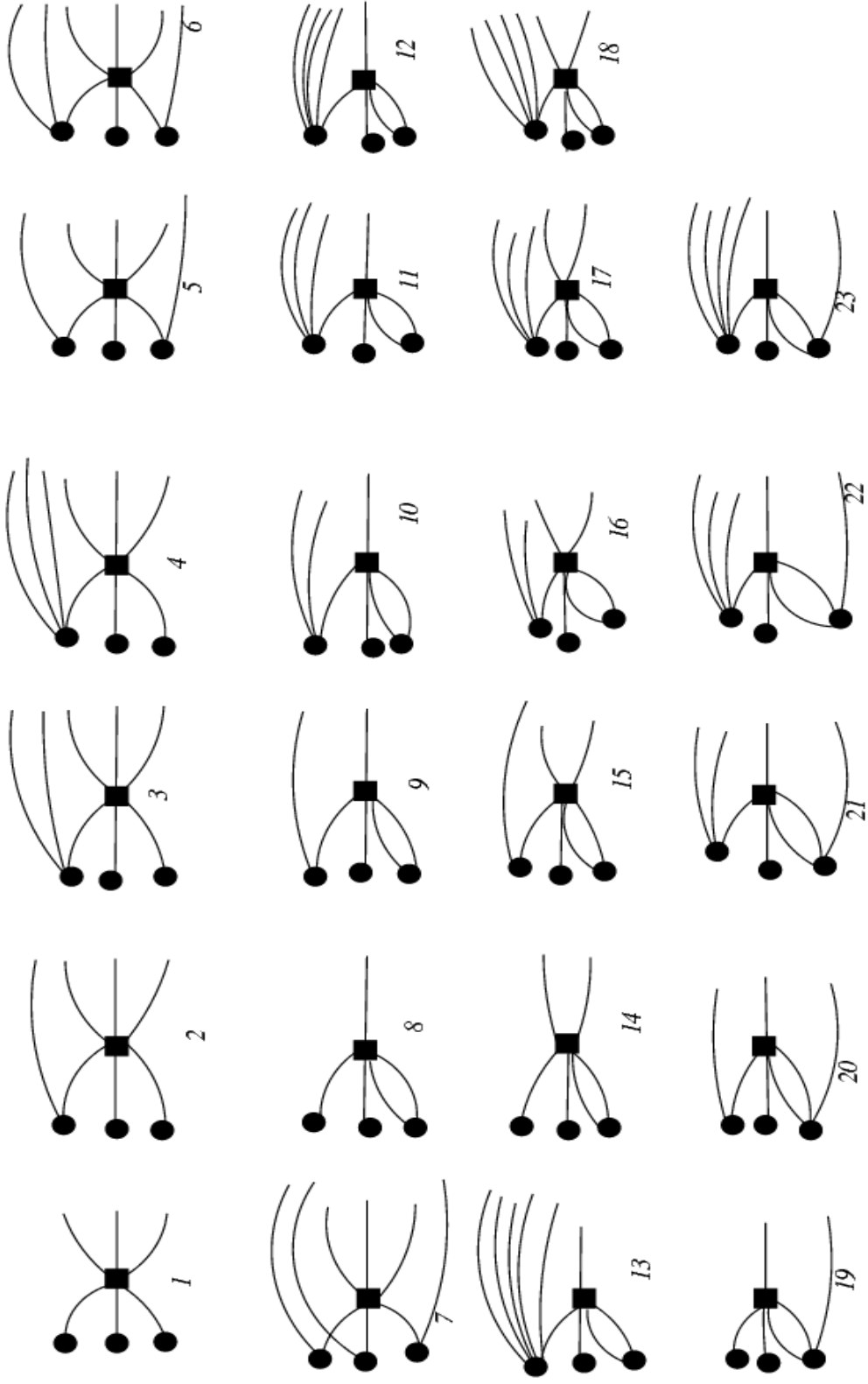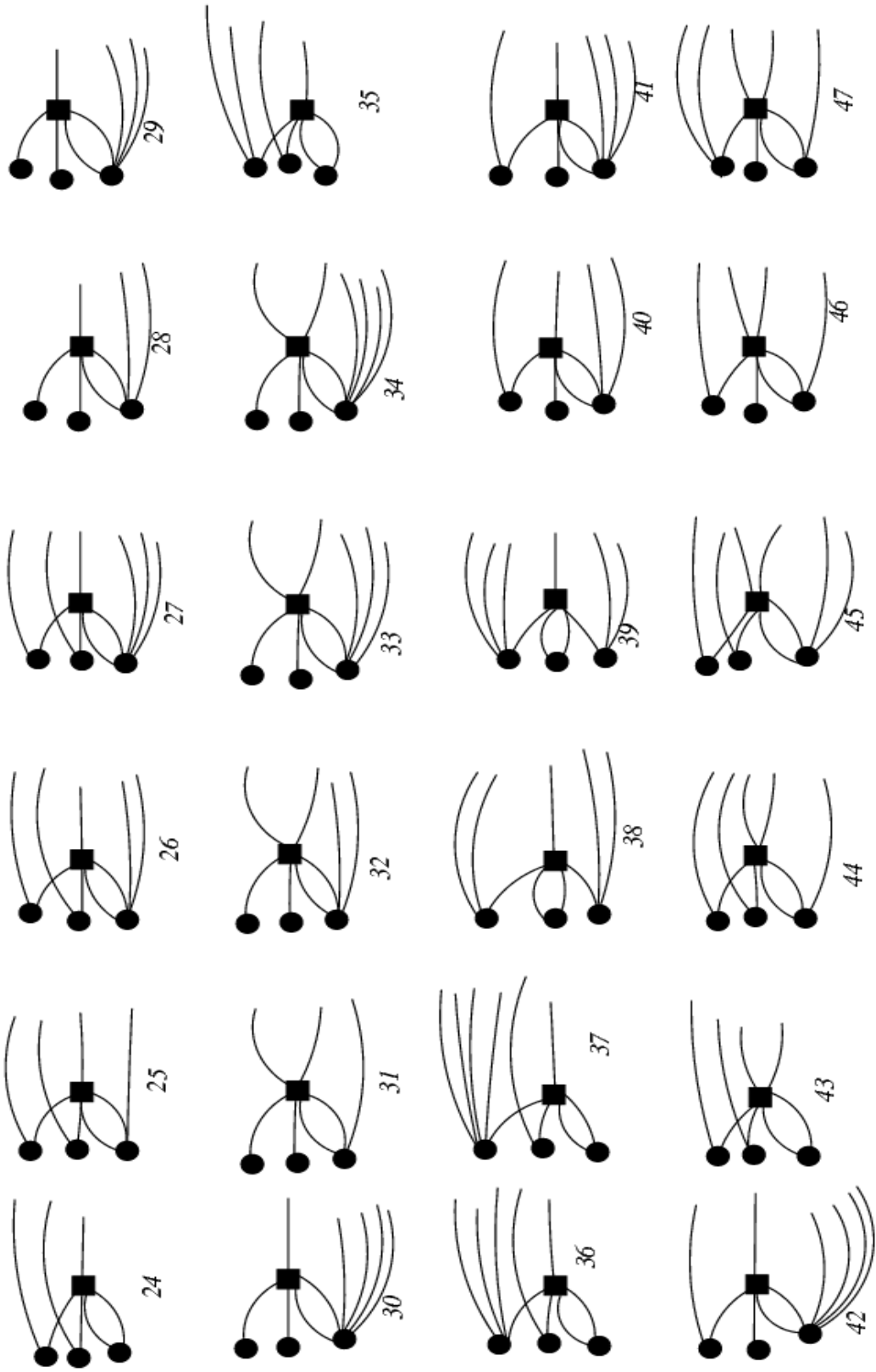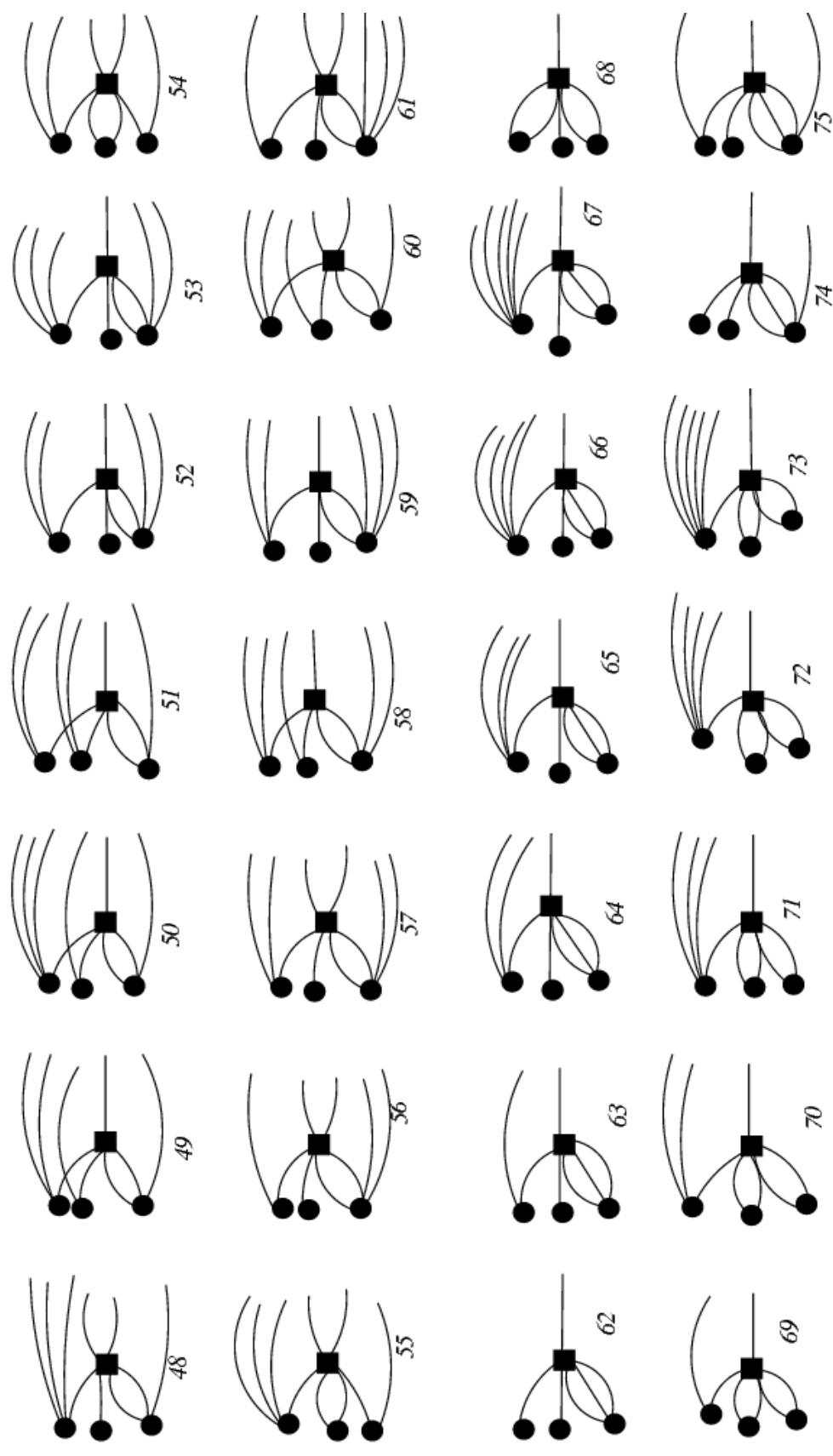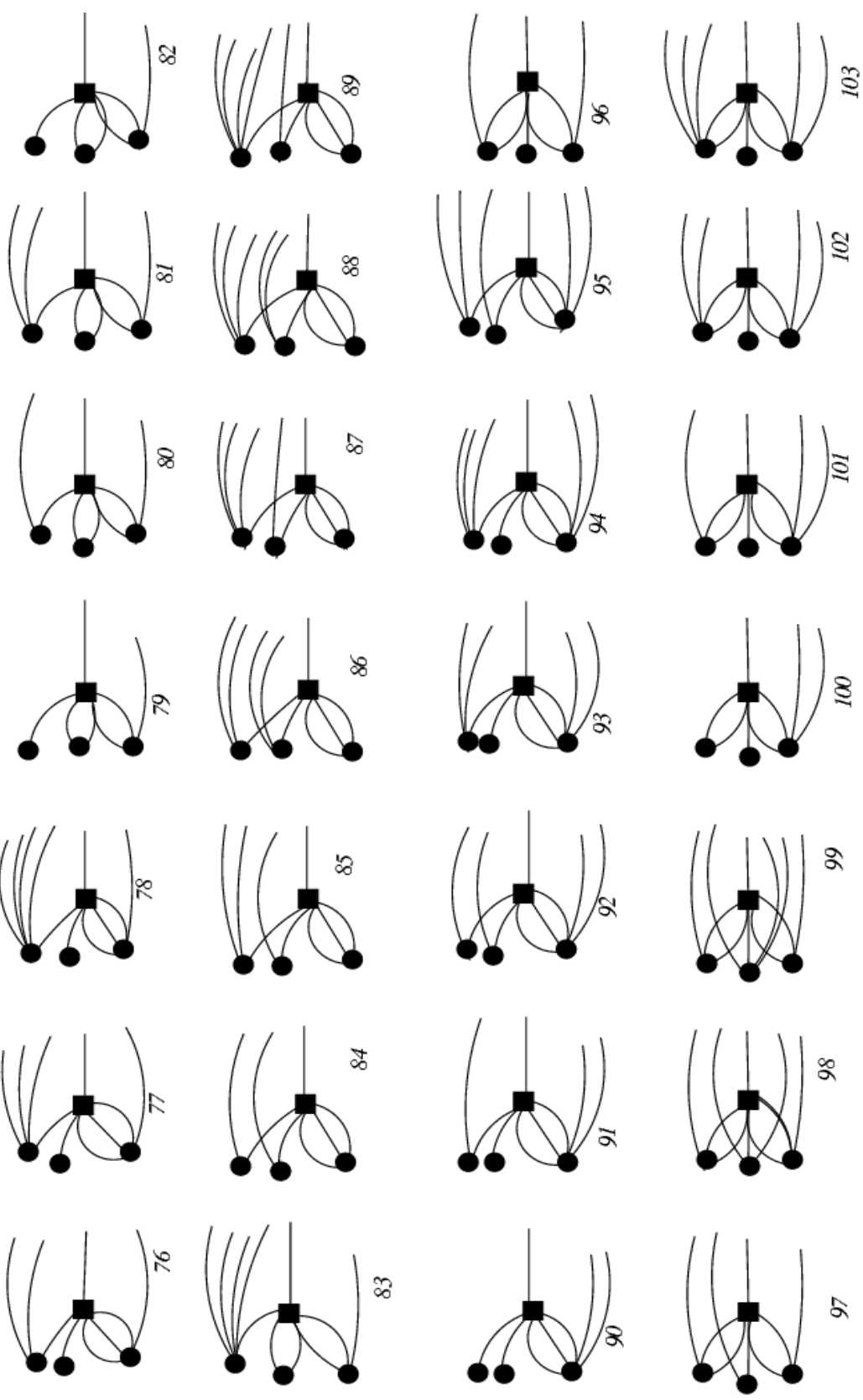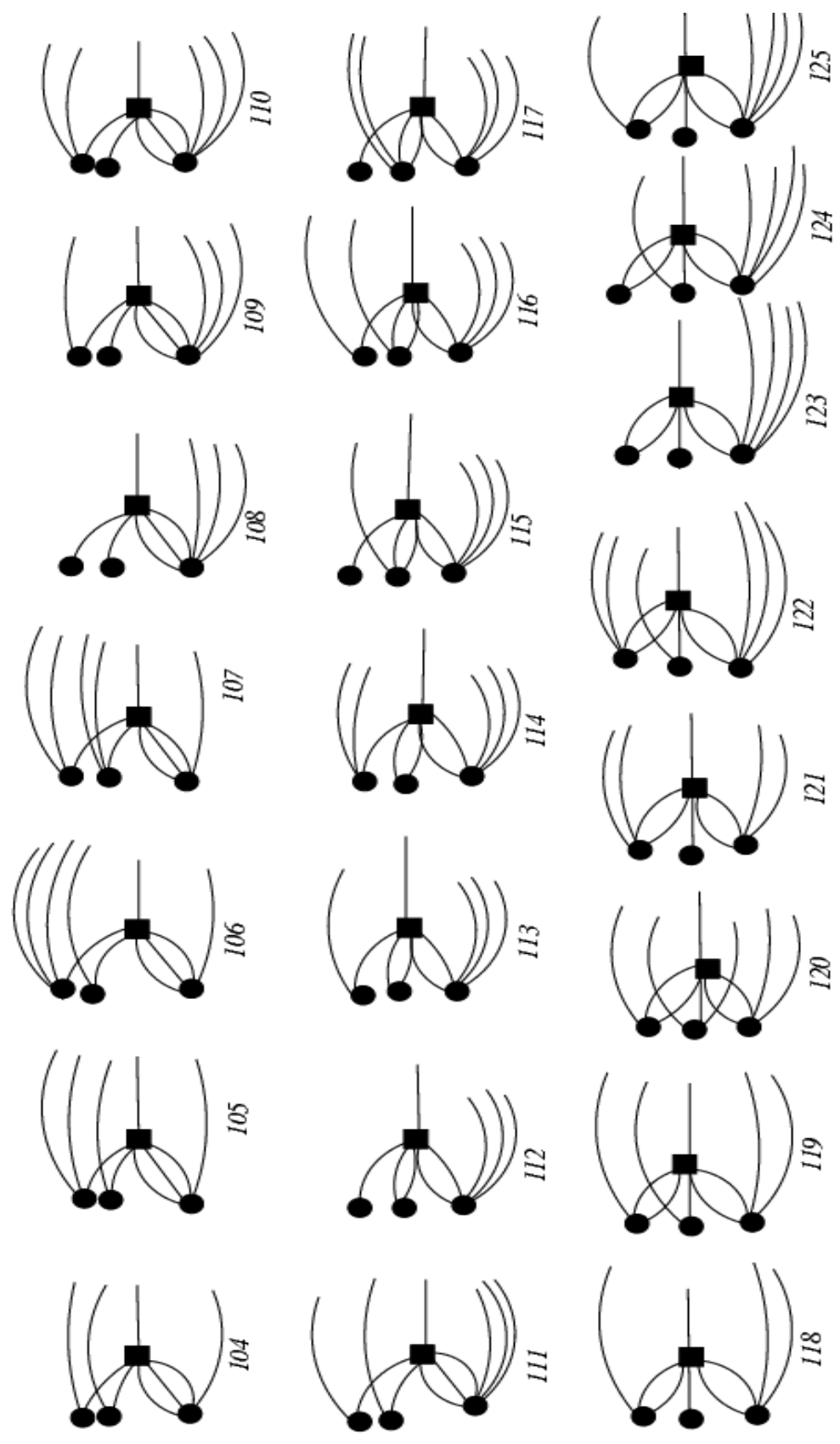
MRCC Diagrams

Four boson approximation

H10 diagrams

S1 diagrams
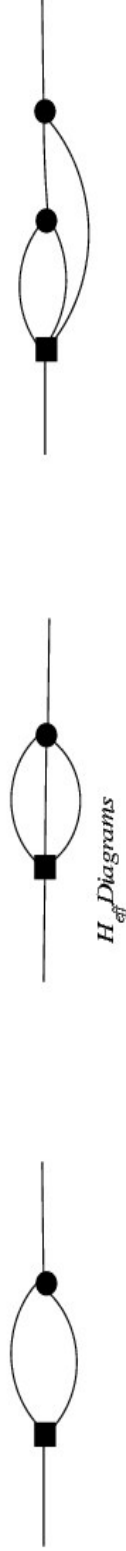
H_eff Diagrams

S₁ Diagrams: Linear Diagrams

1

2

3

4

Quadratic Diagrams

Cubic Diagrams

13   14   15   16   17

18   19   20   21   22

23   24   25   26   27

28   29   30   31   32

33

Quartic Diagrams