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DIPLOMA THESIS



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# Study of Diradicals By Explicitly Correlated Multireference Coupled Cluster Methods

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I am grateful to my parents, for all the support they have given me throughout the whole of my studies.



I proclaim that this diploma thesis was made solely by me and that I have enlisted all the sources of information and literature. I also proclaim that neither this thesis nor a part of it was used to acquire any other academic title.

In Prague on August 23, 2013

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Název práce: Studium diradikálů multireferenčními metodami spřažených klastrů

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Abstrakt: Tematem diplomové práce je studium isomerizace cyklopropánu přes trimetylenový / propylidénový diradikál pomocí jednak konvenční a jednak multireferenční metody vázaných klastrů. Hlavním cílem bylo srovnat konvergenci získaných energií s velikostí použité báze pro konvenční a explicitně korelované MRCC výpočty. Podle očekávání výsledky ukázaly, že explicitní korelace vede k výraznému zlepšení konvergence (cca o jedno kardinální číslo), což umožňuje výrazné úspory výpočetního času. Navíc výpočty pomocí MkCCSD(T)-F12/QZ a BWCCSD(T)-F12/QZ metod patří mezi ty nejs sofistikovanejší, jaké kdy byli na výpočet relativní energií cyklopropánu a trimetylénu / propylidénu použity.

Klíčová slova: explicitně korelované, spřažené klastry, multireferenční, isomerizace cyklopropánu, trimetylén, propylidén



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Abstract: Total energies of cyclopropane, trimethylene, and propylidene were calculated with conventional post-HF CCSD(T), BWCCSD(T), MkCCSD(T) methods and their explicitly correlated alternatives. Main aims of the thesis were to compare the basis set convergence of total energies and relative energies between cyclopropane and trimethylene/propylidene, both at the conventional and the explicitly correlated levels. It was shown that use of explicit correlation accelerates the convergence of the total energy by one order of basis set quality, resulting in considerable savings in computational times. Also, the MkCCSD(T)-F12/QZ and the BWCCSD(T)-F12/QZ calculations belong to the most sophisticated approaches employed for estimation of the relative energies of cyclopropane and trimethylene/propylidene to date.

Keywords: explicitly correlated, coupled cluster, multi-reference, cyclopropane isomerisation, trimethylene, propylidene



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# Introduction

Coupled cluster (CC) method was introduced in the quantum chemistry field by Jiří Čížek in 1966. Since that time, it became one of the most widely used *ab initio* methods in quantum chemistry due to its reliability and accuracy. Two of the multitude of CC variants which have been developed over the years became significantly favoured by the computational community: Coupled Cluster Single and Double excitations (CCSD) method, and Coupled Cluster Single, Double, and Perturbative Triple excitations (CCSD(T)) method. Nowadays, the CCSD(T) approach is considered to be the 'golden standard' of single reference methods.

Even though single reference methods are used in the majority of calculations, chemical systems with quasi-degenerate HOMO and LUMO orbitals, such as biradicals, pose a serious problem for the reliability of their results. In such circumstances, it is more convenient to employ the multi-reference treatment, which substitutes the higher order expansion of the excitation operators required at the single reference level. Incorporation of the multi-reference approach in the coupled cluster method was found to be ambiguous and rather complicated to achieve.

Multi-reference Mukherjee's coupled cluster method (MR MkCC) and multi-reference Brillouin-Wigner coupled cluster method (MR BWCC) both belong to the same class of generalisations of the single reference coupled cluster theory, called Hilbert-space MRCC methods. Main difference between these two

methods is that only the MkCC approach is size-extensive. The lack of size-extensivity of the BWCC method is compensated by size-extensivity corrections.

The single reference as well as the multi-reference generalisation express the wave-function as a linear combination of products of one-electron functions, which leads to slow basis set convergence of energies. Therefore, search for a method able to accelerate the basis set convergence began, with Kutzelnigg being the first to report enhancements in the energy convergence using his explicitly correlated methods.

Explicitly correlated methods (also called F12 methods) include two-electron terms in the correlated wave-function. This explicit dependence of the wave-function on the interelectronic distance,  $r_{12}$ , accounts for a better description of the correlation cusp region of the wave-function, which in turn accelerates the basis set convergence of energy.

Using both the multi-reference treatment and the explicit correlation together yields a method which has the static correlation included at a satisfactory level and has an improved dynamic correlation energy convergence towards the basis set limit. Both single reference and multi-reference, MkCC and BWCC, methods were already generalised with the F12 theory, yielding the CC-F12, MkCC-F12, and BWCC-F12 approaches, respectively.

Main aim of this thesis is to compare the performance of the aforementioned methods on the isomerisation of cyclopropane to propene, which passes through the trimethylene or propylidene diradicals, in terms of basis set convergence of total energy and relative energies.

Organisation of the thesis is as following: Chapter 2 opens with a concise introduction to quantum chemistry, which briefly introduces the fundamental approximations taken when solving the Schrödinger equation. Next, the second quantization formalism and size-extensivity are presented. After that, a section on the electron correlation methods follows, with focus on coupled cluster approaches. Then the key elements of the explicitly correlated approach are presented. Chapter 2 concludes with the multi-reference and the F12 generalisations of the single reference coupled cluster approach. Chapter 3 is devoted to the study of the isomerisation of cyclopropane to propene through trimethylene/propylidene. After the principal literature results are described,

the computational details follow. After that, all our results are presented and compared with the literature results. Chapter 4 contains the conclusions of our work.



# Theory

This chapter provides an overview on some of the quantum chemistry *ab initio*<sup>1</sup> methods. The main purpose of this chapter is to present the most important aspects of the the *coupled cluster* approach and the *explicitly correlated* methods.

The first part of this chapter introduces essential concepts of quantum chemistry, which are then used throughout the thesis. The second part contains some general information about standard *ab initio* methods, with the focus directed towards the Coupled Clusters (CC), as well as their multi-reference generalisation. The third part is focused on the multi-reference Brillouin-Wigner and Mukherjee's Coupled Cluster Singles and Doubles (MR BWCCSD and MR MkCCSD) with explicit correlation (F12) approach. Detailed information on these topics can be found in the literature [1, 2, 3, 4, 5, 6, 7, 8].

## Background of Computational Chemistry

Computational chemistry methods aim at the elucidation of molecular structure and properties of many-electron molecular systems and their reactivity. The plethora of the approaches devised can be grouped into several categories: *molecular mechanics* based, *density* based, *molecular dynamics* based and, finally, *wave-function* based methods.

<sup>1</sup>*ab initio* means "from first principles". The rationalisation for this name comes from the fact that these methods are based only on the basic physical theory - the quantum mechanics.

The motivation to extract chemical knowledge using the tools of computational chemistry comes from the fact that performing calculations is cheaper and generally faster than performing the experiments. Also, using computer calculations in chemistry often provides reliable information on the feasibility of an experiment.

Among the typical pursuits of computational chemistry are the determination of the molecular geometry, computation of the energies of molecules and transition states, the extraction of information about the chemical reactivity of the molecules, and establishing physical properties of molecules.

This thesis is concerned with the wave-function approaches.

## The Schrödinger Equation

The non-relativistic, time-independent Schrödinger equation is central for the conventional *ab initio* methods:

$$\hat{H}\psi_i = E_i\psi_i, \quad (2.1)$$

where  $\hat{H}$  is the Hamiltonian,  $E_i$  is the energy and  $\psi_i$  is the wave function.

The purpose of solving Equation 2.1 is to extract the energy of the system and often also to determine the wave function of stationary states. Knowing the wave function is of major importance because it contains information from which any property of the system can be computed (at least in theory).

That being said, the inconvenient truth is that exact solutions of the Schrödinger equation exist only for the simplest model systems such as the harmonic oscillator or any one-electron species. Approximations need to be administered for any system with more than one electrons.

## The Approximations

The major approximations being used are the Born-Oppenheimer approximation, the Hartree-Fock approximation, i.e. the replacement of the exact wave-function with a Slater determinant and the utilisation of a basis set.

The Born-Oppenheimer approximation separates the nuclear and the electronic motion based on the difference in their masses. It enables us to solve the Schrödinger equation for an electronic problem with fixed nuclear coordinates, simplifying the solution of the  $n$ -electron equation into two separate steps.

The Hartree-Fock (HF) approximation treats the movement of electrons in an averaged way. In other words, it does not correlate the electronic motion with respect to each other. Within the Hartree-Fock method, the *true* wave function is approximated by one Slater determinant (SD). HF approximation is generally too crude and thus serves only as a first step for subsequent correlated calculations.

The SD is an *antisymmetrized* product of *spinorbitals*. Orbitals are one-electron wave functions. In the Hartree-Fock approach, they are expanded into a set of basis functions centered on the atomic nuclei. If the expansion was being made into a complete set, the orbitals would in principle be exact. However, the expansion set always has to be truncated at some point and therefore another approximation is being made - the *basis set* approximation.

## Second Quantization

Second quantization is particularly well suited to be used within the domain of the *electron correlation* methods, which constitute the follow-up to the Hartree-Fock method.

Techniques of second quantization constitute an alternative formalism directed towards a compact and convenient notation of operators and wave-functions. The distinguishing feature of second quantization is expressing the operators irrespective of the number of particles.

The usual convention that is also going to be adapted in this thesis, is that the letters  $i, j, k, \dots$  represent the occupied spinorbitals (the *hole states*), the letters  $a, b, c, \dots$  signify the unoccupied spinorbitals (the *particle states*), and the letters  $p, q, r, \dots$  refer to an unspecified spinorbital (any of the two states).

The means by which second quantization achieves its goals are the *creation* and *annihilation* operators. To demonstrate this, let us have an orthonormal

one-particle basis:

$$\{\phi_i\} = \{\phi_1, \phi_2, \dots\}; \quad \langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (2.2)$$

In such a basis, the Slater determinant  $\Phi$  has the representation:

$$\Phi = \Phi_{ijk\dots z} \equiv |\phi_i \phi_j \phi_k \dots \phi_z\rangle \equiv |ijk\dots z\rangle \quad (2.3)$$

The definition of the creation and annihilation operators is with respect to their action on SDs:

$$\hat{a}_p^\dagger |qr\dots z\rangle = |pqr\dots z\rangle, \quad (2.4)$$

$$\hat{a}_p |pqr\dots z\rangle = |qr\dots z\rangle. \quad (2.5)$$

So the creation operator  $\hat{a}_p^\dagger$  creates an electron in an empty spinorbital  $\chi_p$ . The annihilation operator  $\hat{a}_p$ , on the other hand, removes an electron from the spinorbital  $\chi_p$ .

These operators enable us to construct an arbitrary SD by consecutive application of a string of creation operators  $\hat{a}_p^\dagger$  on the *vacuum* state  $|\rangle$ , which is formally defined as a determinant without any spinorbitals<sup>2</sup>:

$$\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r^\dagger \dots \hat{a}_z^\dagger |\rangle = |pqr\dots z\rangle. \quad (2.6)$$

Furthermore, the  $\hat{a}_p^\dagger$  and the  $\hat{a}_p$  operators satisfy the *anticommutation relations*:

$$\begin{aligned} [\hat{a}_p, \hat{a}_q]_+ &= [\hat{a}_p^\dagger, \hat{a}_q^\dagger]_+ = 0 \\ [\hat{a}_p^\dagger, \hat{a}_q]_+ &= [\hat{a}_p, \hat{a}_q^\dagger]_+ = \delta_{pq}. \end{aligned} \quad (2.7)$$

A *reference state* is introduced in order to simplify the expressions for SDs:

$$|0\rangle \equiv |\Phi_0\rangle = |ijk\dots n\rangle. \quad (2.8)$$

<sup>2</sup> with N = 0.

The SDs are then defined with respect to this reference state, also called the *Fermi vacuum*, as for example:

$$|\Phi_i^a\rangle \equiv \hat{a}_a^\dagger \hat{a}_i |\Phi_0\rangle = |ajk \cdots n\rangle \quad (\text{single excitation}) \quad (2.9)$$

$$|\Phi_{ij}^{ab}\rangle \equiv \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j |\Phi_0\rangle = |abk \cdots n\rangle \quad (\text{double excitation}) \quad (2.10)$$

Operators of the one- and two-electron physical quantities have the following form in the second quantization formalism:

$$\hat{O}_1 = \sum_{pq} \langle p|O_1|q\rangle \hat{a}_p^\dagger \hat{a}_q \quad (\text{one - electron}) \quad (2.11)$$

$$\hat{O}_2 = \sum_{pqrs} \langle pq|O_2|rs\rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \quad (\text{two - electron}) \quad (2.12)$$

The Hamiltonian operator, which has a one and a two body part, can be expressed as:

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r, \quad (2.13)$$

with  $h_{pq} = \langle p|h|q\rangle$  and

$$\begin{aligned} \langle pq||rs\rangle &\equiv \langle pq|rs\rangle - \langle pq|sr\rangle = \int \chi_p^*(1) \chi_q^*(2) \frac{1}{r_{12}} \chi_r(1) \chi_s(2) dx_1 dx_2 - \\ &- \int \chi_p^*(1) \chi_q^*(2) \frac{1}{r_{12}} \chi_s(1) \chi_r(2) dx_1 dx_2 \end{aligned} \quad (2.14)$$

Another important notion is the *normal-ordered product*  $N[\hat{A}\hat{B}\hat{C}\dots]$ . A normal-ordered product of creation and annihilation operators  $\hat{A}, \hat{B}, \hat{C}, \dots$  is defined as a product of these operators where all the creation operators are placed left to all the annihilation operators.

Hamiltonian in the *normal-ordered* form can be written as

$$\hat{H}_N = \sum_{pq} f_{pq} N\{\hat{a}_p^\dagger \hat{a}_q\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle N\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\}, \quad (2.15)$$

where  $f_{pq} = \langle p|f|q\rangle$  are the Fock matrix elements.

## Size-Extensivity

Two of the very important properties that any electron correlation method should satisfy are the size-extensivity and the size-consistency.

Methods which exhibit correct (linear) scaling with respect to the number of electrons in the system are called *size-extensive*.

Methods in which the energy of a system consisting of two non-interacting fragments A and B is equal to the sum of the fragment energies calculated separately are called *size-consistent*.

## Electron Correlation Methods

The Hartree-Fock method recovers approximately 99 % of the total energy of a system. However, it is the 1 % of the energy being left out that is crucial in reaching the chemical accuracy<sup>3</sup>, since the relative energies rather than absolute ones are of interest, and the correlation energy undergoes significant changes along the reaction coordinate.

The electron-correlation methods provide means of collecting the energy neglected by Hartree-Fock. Their use is therefore essential if chemical accuracy is to be achieved at all.

Their name clearly points to the fact that they were devised to overcome the natural limitation of the Hartree-Fock method - that the motion of electrons is not correlated. The energy recovered by these methods has been named accordingly - the *correlation energy*.

The correlation methods in standard use include the Moller-Plesset perturbation theory to the second order (MP2), the configuration interaction singles and doubles (CISD), and the coupled cluster singles and doubles (CCSD), or the CCSD(T) approach, which is based on a combination of the perturbation theory and coupled clusters.

<sup>3</sup>I.e. the results being accurate up to 1 kcal/mol or 1.6 miliHartrees.

## The Coupled Clusters Method

Original development of the coupled cluster (CC) method dates back to 1950s and the research domain of nuclear physics [9, 10, 11]. The CC approach was rediscovered in 1966 by Čížek and Paldus, who foresaw its relevance for quantum chemistry as an approach to describe electron correlation, and developed the diagrammatic formalism used to formulate CC equations in a graphical form. [12, 13, 14]. During the 1980s, the attention towards CC was constantly increasing as its advantages began to be recognised. Examples of milestones in the development of CC theory include the prime implementation of the coupled cluster singles and doubles (CCSD) by Purvis And Bartlett in 1982 [15] as well as establishment of the CCSD(T) method by Raghavachari et. al [16] in 1989.

The innovative feature of CC with respect to the CI method is the exponential ansatz for the correlated wave-function:

$$\psi = e^{\hat{T}} \Phi_0. \quad (2.16)$$

Here,  $\exp(\hat{T})$  is a *wave operator* and  $\hat{T}$  is a *cluster operator*. The cluster operator consists of excitation operators of different rank:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N, \quad (2.17)$$

with  $N$  being the total number of electrons in the system and

$$\hat{T}_1 = \sum_{i,a} t_i^a \hat{a}_a^\dagger \hat{a}_i \quad (2.18)$$

being a single excitations operator,

$$\hat{T}_2 = \sum_{\substack{a < b \\ i < j}} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \quad (2.19)$$

describing double excitations and so on.

If we take all these excitation operators into account, they will produce all excited configurations possible with respect to the reference wave-function. Enabling electrons to reach the excited states substantially increases their freedom to move with respect to each other. Therefore, the more excitations are included in a calculation, the more the motions of the electrons will be correlated and

the more correlation energy we will acquire. But since it is practically impossible to perform calculations with a complete set of excitations (except for the smallest systems), the expansion of the cluster operator is always truncated at a specific excitation level.

The amplitudes  $t_i^a, t_{ij}^{ab}, \dots$  correspond to the relative weights of the respective excitations. The aim of the CC method is to determine these amplitudes, and then use them to compute energy or also other properties.

### Formulation and Solution of the CC Equations

Derivation of the CC amplitude equations becomes more convenient by applying  $\exp(-\hat{T})$  on the left side of the Schrödinger equation so that

$$\exp(-\hat{T})\hat{H}_N\exp(\hat{T})\Psi_0 = \Delta E_{corr}\Psi_0. \quad (2.20)$$

From the Baker-Campbell-Hausdorff formula [17] it follows that

$$\begin{aligned} e^{(-\hat{T})}\hat{H}_Ne^{\hat{T}} &= \hat{H}_N + [\hat{H}_N, \hat{T}] + \frac{1}{2!} [[\hat{H}_N, \hat{T}], \hat{T}] + \frac{1}{3!} [[[ \hat{H}_N, \hat{T} ], \hat{T} ], \hat{T}] + \\ &+ \frac{1}{4!} [[[[ \hat{H}_N, \hat{T} ], \hat{T} ], \hat{T} ], \hat{T}]. \end{aligned} \quad (2.21)$$

The next step is to substitute this expansion into the Schrödinger equation 2.20 and project from left by the determinants responsible for the single, double, etc. excitations  $\langle \Phi_{i\dots}^{a\dots} |$  in order to get:

$$\begin{aligned} \langle \Phi_{i\dots}^{a\dots} | \hat{H}_N + [\hat{H}_N, \hat{T}] + \frac{1}{2!} [[\hat{H}_N, \hat{T}], \hat{T}] + \frac{1}{3!} [[[ \hat{H}_N, \hat{T} ], \hat{T} ], \hat{T}] + \\ + \frac{1}{4!} [[[[ \hat{H}_N, \hat{T} ], \hat{T} ], \hat{T} ], \hat{T} ] | \Phi_0 \rangle = 0. \end{aligned} \quad (2.22)$$

The excited determinants are all orthogonal with respect to the reference determinant, yielding zero on the right hand side. The space spanned by the cluster operator determines the number of determinants. As an example, let us take the cluster operator expanded up to double excitations, i.e.  $\hat{T} = \hat{T}_1 + \hat{T}_2$ . As a result, we are provided with two determinant sets to work with,  $\langle \Phi_i^a |$  and  $\langle \Phi_{ij}^{ab} |$ , respectively. The respective equations are

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle = 0 \quad (2.23)$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle = 0. \quad (2.24)$$

For each unknown amplitude there is a matching equation to determine it.

The nonlinearity of the equations follows from (2.22), in which the amplitudes are present up to the fourth order. The procedure for solving the equations is iterative and the starting amplitudes are usually set to zero, leading to MP2 amplitudes after the first CC iteration.

As the final step of the derivation, we separate the linear part of the expression for each of the amplitudes, leaving the other terms on the right hand side:

$$t_i^a(\text{new}) = \frac{1}{D_i^a} \langle \Phi_i^a | \hat{V}_N e^{\hat{T}(\text{old})} | \Phi_0 \rangle \quad (2.25)$$

$$t_{ij}^{ab}(\text{new}) = \frac{1}{D_{ij}^{ab}} \langle \Phi_{ij}^{ab} | \hat{V}_N e^{\hat{T}(\text{old})} | \Phi_0 \rangle. \quad (2.26)$$

The denominators  $D_i^a$  and  $D_{ij}^{ab}$  can be written as:

$$D_i^a = \epsilon_i - \epsilon_a \quad (2.27)$$

$$D_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b, \quad (2.28)$$

with

$$\epsilon_n = \langle \chi_n | f | \chi_n \rangle \quad (2.29)$$

representing the  $n$ -th spinorbital's ( $\chi_n$ ) energy and

$$\hat{V}_N = \hat{H}_N - \sum_p f_{pp} N \{ \hat{a}_p^\dagger \hat{a}_p \} = \sum_{p \neq q} N \{ \hat{a}_p^\dagger \hat{a}_q \} + \frac{1}{2} \sum_{pqrs} \langle pq | rs \rangle N \{ \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \}. \quad (2.30)$$

After the iterative amplitude equations converge and we obtain the amplitudes, the Schrödinger equation is multiplied with the reference determinant  $\langle \Phi_0 |$  to obtain the energy equation:

$$\Delta E_{corr} = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle. \quad (2.31)$$

### Comparison of the CC and CI methods

The configuration interaction (CI) approach uses linear combination of Slater determinants for expansion of the wave-function. The CI wave operator is taken in the form

$$\hat{\Omega}_{CI} = 1 + \sum_i \hat{C}_i = 1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \dots, \quad (2.32)$$

where the single and the double excitation operators are

$$\hat{C}_1 = \sum_{ia} c_i^a \hat{a}_a^\dagger \hat{a}_i \quad (2.33)$$

$$\hat{C}_2 = \sum_{i < j} \sum_{a < b} c_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i. \quad (2.34)$$

Higher excitation operators are defined analogously.

The CI and the CC method share a common feature in the usage of a series of excited Slater determinants to expand the wave-function. Comparison of the wave operators of these two methods provides useful relationships between the excitation operators  $\hat{C}_n$  and  $\hat{T}_n$ :

$$\begin{aligned} \hat{C}_1 &= \hat{T}_1, \\ \hat{C}_2 &= \hat{T}_2 + \frac{1}{2!} \hat{T}_1^2, \\ \hat{C}_3 &= \hat{T}_3 + \frac{1}{3!} \hat{T}_1^3 + \hat{T}_1 \hat{T}_2, \\ \hat{C}_4 &= \hat{T}_4 + \frac{1}{4!} \hat{T}_1^4 + \frac{1}{2!} \hat{T}_2^2 + \hat{T}_1 \hat{T}_3 + \frac{1}{2!} \hat{T}_1^2 \hat{T}_2, \\ &\dots \end{aligned} \quad (2.35)$$

Note that for the cluster operator in the form  $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n$ , all the CI operators contributions  $\hat{C}_n$  are automatically included in the wave-function. The operator  $\hat{T}_n$  additionally includes contributions from higher orders of the expansion. These higher-order contributions are a direct result of the exponential character of the CC excitation operator. That is why the CCSD method includes some contributions from triple excitations and the principally contributing quadruple excitations as well. On the other hand, the CISD method includes exclusively single and double excitations.

The CCSD method, scaling as  $\mathcal{O}(n^6)$ , is computationally more demanding than the corresponding CISD method, which scales as  $\mathcal{O}(n^5)$  with respect to the system size. However, the important difference is that the CCSD wave-function is close to CISDTQ wave-function in quality, which has the scaling of  $\mathcal{O}(n^9)$ .

## Explicitly Correlated Methods

Besides the excitation level, accuracy of the wave-function methods is limited by their slow convergence with respect to the orbital expansion. This lack of faster convergence together with highly increasing computer resources with the increasing size of the basis set has led to a search for novel approaches. Among these approaches, the methods with explicit correlation hold a prominent place.

Let us consider an example in order to gain a more specific idea about the speed of the convergence of the conventional wave function approaches. One of the bottlenecks for the computational time of the wave-function calculations is the evaluation of the four-index two-electron integrals, which scales as (at least)  $t = \mathcal{O}(m^4)$ , where  $m$  is the number of basis set functions. Now, the inaccuracies in correlation energies diminish as  $\epsilon = \mathcal{O}(m^{-1})$  [18, 19]. Combining these two dependencies together, we acquire a relation between the error in correlation energies and the computational time, as  $\epsilon = \mathcal{O}(t^{-1/4})$ . This means that the increase of computational time by a factor of 10 000 will guarantee just an order of magnitude improvement in precision.

This slow convergence problem is improved upon in explicitly correlated methods by incorporating the inter-electronic distances in the correlated wave-function. Inclusion of such  $r_{12}$  terms inside the wave function deals with the difficulty of representing the cusp feature of the wave-function, as formulated by Kato [20]:

$$\lim_{r_{12} \rightarrow 0^+} \left( \frac{\partial \Psi}{\partial r_{12}} \right) = \frac{1}{2} \Psi(r_{12} = 0). \quad (2.36)$$

The meaning of this cusp condition is clarified when the Coulomb interaction is taken into consideration. The Coulomb interaction is divergent for two electrons approaching each other. But since the local energy<sup>4</sup> should be constant everywhere for an exact wave-function, the kinetic energy term has to compensate for the diverging electron-electron repulsion term. This yields the asymptotic behaviour described in Equation 2.36.

<sup>4</sup>i.e. the energy at a specific point on the PES

The first example justifying the use of the explicit correlation approach came from the investigation of two-electron systems by E. A. Hylleraas. He was the first to use wave-functions with  $r_{12}$  terms [21] such as:

$$\Psi(\vec{r}_1, \vec{r}_2) = e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} \sum_{klm} C_{klm} (\vec{r}_1 + \vec{r}_2)^k (\vec{r}_1 - \vec{r}_2)^l r_{12}^m. \quad (2.37)$$

While the usefulness of these Hylleraas type wave-functions was invaluable for two-electron species, its applicability to larger systems was hindered by the need to solve three- and four-electron integrals. Not only they are frequently not solvable in analytic form, but also there is as many as  $\mathcal{O}(m^6)$  and  $\mathcal{O}(m^8)$  three- and four-electron integrals, respectively, with  $m$  being the number of functions used in the orbital expansion. Evaluation of these integrals for any but the smallest systems poses an intimidating computational challenge.

Three different strategies have been proposed to escape from the need to compute all of these three- and four-electron integrals: the transcorrelated method of Boys [22], the weak orthogonality functional of Szalewicz *et al.* [23, 24], and the R12 approaches by Kutzelnigg and Klopper [25, 26]. Among these, it is the R12 approaches that dominate the field nowadays.

The key feature of the R12 methods of Kutzelnigg and Klopper was the use of conventional expansion supplemented by only a small number of explicitly correlated basis functions, such that:

$$\Psi_{R12} = \Phi_{HF} + \sum_{\substack{a < b \\ i < j}} a_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i < j} b_{ij} f_{12} \Phi_{HF}, \quad (2.38)$$

where  $\Phi_{HF}$  is the Hartree-Fock determinant,  $\Phi_{ij}^{ab}$  is a determinant describing double excitations, and  $a_{ij}^{ab}$  and  $b_{ij}$  are the relative weights of the determinants<sup>5</sup>, and  $f_{12}$  is the correlation factor. In almost all of the early works the correlation factor was chosen as  $r_{12}$ , the inter-electronic distance. This approach was fruitful for quite a lot of larger systems as well, including water tetramer [27], ferrocene [28], annulene [29], and the benzene dimer [30].

In spite of these successes, this linear correlation factor still had its disadvantages. Namely, the difficulty of solving the three- and four-electron integrals remained as they could not be dealt with analytically. Also, the  $r_{12}$  factor

<sup>5</sup>This form of R12 wave function is only illustrative as it is neither antisymmetrized yet nor projected onto the actual basis.

was providing the correct wave-function only for very small inter-electronic distances, whereas it exhibited erroneous behaviour for longer ranges.

These complications inspired a search for more suitable correlation factors. Persson and Taylor [31, 32] expanded the linear term by fitting a number of Gaussian geminals onto it. Samson with coworkers [33] multiplied the  $r_{12}$  term with a Gaussian function in order to damp it. But the major breakthrough came when Ten-no [34] proposed the use of a Slater-type geminal, such that:

$$f_{12} = 1 - \exp(-\gamma r_{12}) = \gamma r_{12} + \mathcal{O}(r_{12}^2), \quad (2.39)$$

where  $\gamma$  is an arbitrary exponent that needs to be optimised. This STG factor provided excellent results and inspired more research in this area [35, 36].

The only major obstacle that had to be solved within the R12/F12 methods was to cope with solving the vast number of three- and four-electron integrals. It was Kutzelnigg again who came up with an ingenious idea to approximate such integrals using a resolution of identity (RI). In order to apply the RI, the generalised and extended Brillouin conditions (depending on the type of projector used) are employed. Such a treatment is referred to as 'standard approximation' (SA) and it was introduced by Kutzelnigg and Klopper [26].

The practical implementation of the SA, known as the standard approximation A, is distinguished by neglecting the exchange commutator altogether:

$$[\hat{K}_{12}, f_{12}] \approx 0, \quad (2.40)$$

and it requires single RI insertions only.

On the other hand, in standard approximation B, the exchange commutator is calculated accurately.

Noga *et al.* introduced a less complicated method, which they called standard approximation C [37]. Its idea is to isolate the exchange part from the Fock operator. Standard approximation C is more accurate than both the SA A and SA B because no other approximation apart from RI is required, and easier to implement.

The formula representing the resolution of identity

$$\hat{1} = \sum_p^\infty |\phi_p\rangle\langle\phi_p| = \sum_{pqr}^\infty |\phi_p\phi_q\phi_r\rangle\langle\phi_p\phi_q\phi_r|, \quad (2.41)$$

transform the three- and four-electron integrals into products of two-electron integrals provided that we expand the MOs in a complete basis set.

Moreover, the disadvantage of the RI approach was that it required very large basis sets to be accurate enough. In order to tackle this problem, Klopper and Samson introduced the use of an 'auxiliary basis set' (ABS) method [38]. An alternative approach was devised by directly approximating the orthogonal projector  $1 - \hat{P}$ :

$$\hat{X} = 1 - \hat{P} \approx \hat{X}' = \sum_{p_\perp} |p_\perp\rangle\langle p_\perp|, \quad (2.42)$$

where  $\hat{X}'$  is an approximate projector on the orthogonal complement to the given basis. This comprises the core of the 'complementary' ABS approach (CABS) [39].

With all the primary features of the explicitly correlated methods laid down, let us stress once more how dramatic improvement they provide in terms of energy convergence. The error of the energy with reference to the basis set limit is improved from  $(L + 1)^{-3}$  scaling [40] for the conventional wave-function approaches to  $(L + 1)^{-7}$  [41] in R12/F12 theories, where  $L$  is the highest angular momentum present in the basis.

With the advantages the R12/F12 approaches offer, it was only a question of time until they have been implemented into the codes of the conventional methods. Let us mention the CISD [42], CCSD [43, 44] and multi-reference configuration interaction (MRCI) [45] wave functions as examples.

We shall present the essentials of the formulation of the CCSD-F12 method [46].

The exponential ansatz for the CCSD-F12 wave function can be written as:

$$\Psi = e^{\hat{S}}\Phi_0, \quad (2.43)$$

where  $\Psi$  is the exact wave function and  $\Phi_0$  is the reference Hartree-Fock wave function. The operator  $\hat{S}$  consists of two parts:

$$\hat{S} = \hat{T} + \hat{\mathcal{R}}, \quad (2.44)$$

where  $\hat{T}$  is the cluster operator from the conventional theory and  $\hat{\mathcal{R}}$  deals with an appropriate characterisation of the correlation cusp. We are going to focus on the expansion and properties of  $\hat{\mathcal{R}}$  here.

In the following, indices  $i, j, k, \dots$  label the occupied spin orbitals,  $a, b, c, \dots$  denote the virtual spin orbitals, and  $\alpha, \beta, \gamma, \dots$  designate the virtual spin orbitals inside the orthogonal complement to the computational basis.

Inclusion of  $\hat{\mathcal{R}}$  inside the CC formalism corresponds to a formal extension of the basis by functions which sufficiently describe the correlation cusp. Structure of the operator  $\hat{\mathcal{R}}$  is essentially the same as the  $\hat{T}_2$  operator, the difference being that the summation runs through the orthogonal complement,  $\alpha, \beta$ , to the computational basis  $a, b$ . The operator  $\hat{\mathcal{R}}$  is defined as [47]:

$$\hat{\mathcal{R}} = \frac{1}{4} c_{kl}^{ij} \hat{\mathcal{R}}_{ij}^{kl}, \quad \hat{\mathcal{R}}_{ij}^{kl} = \frac{1}{2} \left( \bar{r}_{\alpha\beta}^{kl} \tilde{a}_{ij}^{\alpha\beta} - \bar{r}_{ab}^{kl} \tilde{a}_{ij}^{ab} \right), \quad (2.45)$$

$$\tilde{a}_{rs}^{pq} = N \{ a_p^\dagger a_q^\dagger a_r a_s \}, \quad \bar{r}_{pq}^{rs} = \langle pq | F(r_{12}) | rs \rangle - \langle pq | F(r_{12}) | sr \rangle, \quad (2.46)$$

where  $F(r_{12})$  is the correlation factor.

Derivation of the CC-F12 equations follows the same pattern as in the conventional CC theory. However, in addition to the customary CC projections of the Schrödinger equation of excited determinants formed within the computational basis, we end up with projections which are due to the newly introduced  $\hat{\mathcal{R}}$  operator as well:

$$\langle \Phi_{a\dots}^{i\dots} | e^{-\hat{S}} H_N e^{\hat{S}} | \Phi_0 \rangle = 0, \quad (2.47)$$

$$\langle \Phi_0 | (\hat{\mathcal{R}}_{ij}^{kl})^\dagger e^{-\hat{S}} H_N e^{\hat{S}} | \Phi_0 \rangle = 0. \quad (2.48)$$

Let us quickly repeat what approximations are required in order to deal with the integrals in equation (2.45). The resolution of identity is the single most important approximation applied. Also, terms scaling as  $(L+1)^{-8}$  are eliminated immediately. Furthermore, within the standard approximation, all terms of  $\hat{\mathcal{R}}$  with open or connected<sup>6</sup> particle lines to  $\hat{T}$  are discarded.

Main difference between the conventional CCSD and the CCSD-R12/CCSD-F12 equations are the two-fold double excitations - not only into the orbitals

<sup>6</sup>This terminology is used in the diagrammatic formalism of CC. It is beyond the scope of this thesis to go into detail about this formalism.

(by  $\hat{T}$ ) but also into the F12 geminals (by  $\hat{\mathcal{R}}$ ). The iterative nature of solving the equations as well as the size extensivity and other properties of the conventional CCSD procedure are preserved.

Ten-no proposed a considerable simplification of the CCSD-F12 equations [48, 49], in which instead of fully optimising the F12 amplitudes during a calculation, they were rather predetermined to comply with the cusp conditions of the wave function [20, 50]:

$$C_{kl}^{ij} = \frac{3}{8}\delta_{ik}\delta_{jl} + \frac{1}{8}\delta_{jk}\delta_{il}. \quad (2.49)$$

The conventional amplitudes of  $\hat{T}$  are then optimised while the F12 coefficients are held *fixed*. This so-called SP approach (i.e. based on SP ansatz [51, 52, 53]) is more tolerant towards the errors resulting from the RI approximations, and thus allows smaller basis sets to be used. Other advantages of the fixed F12 amplitudes formalism are orbital invariance, and lack of singularities and basis set superposition error [54]. The deterioration of accuracy due to the fixation of the F12 coefficients as opposed to their optimisation are insignificant for valence-shell correlation.

Considering the cost of computation, the CCSD-F12 method is slightly more expensive than the conventional CCSD approach. To be more specific, the F12 calculation includes terms with  $\mathcal{O}(O^3X^3)$  scaling, where  $O$  represents the number of occupied orbitals and  $X$  the number of CABS orbitals provided for the RI. Size of the CABS basis is normally two to three times larger than the orbital basis. Compared with the conventional CCSD scaling of  $\mathcal{O}(O^2V^4)$ , where  $V$  stands for the number of virtual orbitals, it might be concluded that the additional computational cost of the F12 calculation comes from the use of the CABS basis set. For comparison, the version of the CCSD-F12 in which the amplitudes are calculated only once and henceforth fixed scales as  $\mathcal{O}(O^2V^2X^2)$ .

## Multireference Coupled Cluster Methods

The conventional single-reference coupled cluster approaches display a relatively inadequate description of non-dynamical correlation if truncation of the cluster operator allows only for low level excitations. Importance of non-dynamical correlation for many systems of chemical interest was a driving force behind the search for methods that would treat the non-dynamical cor-

relation especially well. One of the devised approaches was to use multi-reference treatment.

Multi-reference (MR) methods constitute a different approach for the recovery of the correlation energy. As their name suggests, they incorporate multiple references into the calculation so that no relevant reference configurations of the electrons are left out. Multi-reference approaches are most suitable for systems such as transition-metal compounds, bond breaking processes or biradical species.

While results of the same quality can be achieved by single-reference (SR) approaches as well, the usefulness of the multi-reference approach lies in the effectiveness of the computations for the aforementioned systems. It is true that the SR methods are able to reach the same accuracy as the MR methods, but it requires the expansion of the cluster operator to be sufficiently large, which is not always computationally feasible.

Genuine multi-reference coupled cluster (MRCC) approaches fall into either of the two main categories: *Fock-space CC* (FS-CC) and *Hilbert-space CC* (HS-CC). HS-CC is further split into the *state-universal* (SU) or the *state-specific* (SS) type. This thesis will focus on the HS-CC methods.

The SU HS-MRCC is based on treating multiple electronic states at the same time. The energies of all the states and the corresponding weight coefficients are obtained through the diagonalization of the effective Hamiltonian.

One of the inconveniences of the SU HS-MRCC methods is the emergence of the so called intruder states in the calculations. Intruder states are manifested by a combination of orbital energies yielding a value of the denominators  $D_i^a$  and  $D_{ij}^{ab}$ , in equations (2.25) and (2.26) close to zero, which hampers the convergence of the CC equations.

State-specific HS-MRCC methods focus solely on one of the electronic states at a time. The problem of intruder states is circumvented by a denominator shift applied in these approaches. Characteristic examples of the SS HS-MRCC methods include the Brillouin-Wigner BW-MRCC [55], the Mukherjee Mk-MRCC [56], and the MRexpT ansatz by Hanrath [57].

In the following, both the Mukherjee and the Brillouin-Wigner methods

will be discussed more thoroughly.

## Multireference Brillouin-Wigner Coupled Clusters Method

The Multireference Brillouin-Wigner Coupled Clusters (MR-BWCC) method is based on the Brillouin-Wigner perturbation theory. Derivation of the working equations is presented in the following.

We begin with the generalisation of the reference function to account for the multi-reference character

$$\Phi = \sum_{\mu=1}^M C_{\mu} \Phi_{\mu}, \quad (2.50)$$

meaning that there are  $M$  reference configurations  $\Phi_{\mu}$  forming the basis of the model space.

As the next step, we define a projector operator,  $\hat{P}$ , on the model space

$$\hat{P} = \sum_{\mu=1}^M \hat{P}_{\mu} = \sum_{\mu=1}^M |\Phi_{\mu}\rangle \langle \Phi_{\mu}|, \quad (2.51)$$

where  $\hat{P}$  is the sum of the projectors operating on the reference configurations  $\Phi_{\mu}$ .

The *effective Hamiltonian operator* is introduced by the requirement that it reproduces the exact energy,  $E$ , when acting on the reference function  $\Phi$ :

$$\hat{H}^{\text{eff}} \Phi = E \Phi. \quad (2.52)$$

We can express the effective Hamiltonian utilising the wave and projection operators as

$$\hat{H}^{\text{eff}} = \hat{P} \hat{H} \hat{\Omega} \hat{P}. \quad (2.53)$$

Utilisation of the Bloch equation, which is the next step of the derivation, establishes a connection between the coupled cluster theory and the Brillouin-Wigner perturbation theory. We use the Brillouin-Wigner form of the Bloch equation for the wave operator  $\hat{\Omega}$ :

$$\hat{\Omega} = 1 + \hat{B} \hat{V} \hat{\Omega}, \quad (2.54)$$

in which

$$\hat{B} = \frac{\hat{Q}}{E - \hat{H}_0} = \sum_{q>M} \frac{|\Phi_q\rangle\langle\Phi_q|}{E - E_q}. \quad (2.55)$$

The summation is restricted by the condition  $q > M$ , effectively excluding the internal excitations which convert the references between each other.  $E$  stands for the exact energy, while  $E_q$  are the unperturbed energies that correspond to  $\Phi_q$ .

To obtain a HS-CC method, the wave operator is assumed in the Jeziorski-Monkhorst form [58]:

$$\hat{\Omega} = \sum_{\mu=0}^M e^{\hat{T}(\mu)} \hat{P}_\mu, \quad (2.56)$$

where  $\hat{T}(\mu)$  represents the cluster operator acting on the configuration  $\Phi_\mu$ . Relation (2.56) converts the determination of the correlated wave-function into a task of finding the cluster amplitudes.

Let us express the effective Hamiltonian in a matrix representation spanning the model space

$$H_{\mu\nu}^{\text{eff}} = \langle\Phi_\mu|\hat{H}^{\text{eff}}|\Phi_\nu\rangle = \delta_{\mu\nu}\langle\Phi_\mu|\hat{H}|\Phi_\nu\rangle + \langle\Phi_\mu|\hat{H}_N(\nu)e^{\hat{T}(\nu)}|\Phi_\nu\rangle. \quad (2.57)$$

The only eigenvalue of  $H^{\text{eff}}$  with a physical significance is the exact energy  $E$ . The corresponding eigenvector is formed by the  $C_\mu$  coefficients from equation (2.50).

Next, we employ the Bloch equation in order to derive the cluster amplitude equations.

$$(E - \langle\Phi_\mu|\hat{H}|\Phi_\mu\rangle)\langle\Phi_q|e^{\hat{T}(\mu)}|\Phi_\mu\rangle = \langle\Phi_q|\hat{H}_N(\mu)e^{\hat{T}(\mu)}|\Phi_\mu\rangle, \quad (2.58)$$

where  $\Phi_q$  is an arbitrary excited determinant and  $\Phi_\mu$  is the reference configuration.

If  $\Phi_q$  is singly-excited with respect to  $\Phi_\mu$ , i.e.:

$$\Phi_q = (\Phi_\mu)_i^a, \quad (2.59)$$

then by the substitution of equation (2.59) into equation (2.58) and by observing that

$$\langle(\Phi_\mu)_i^a|e^{\hat{T}(\mu)}|\Phi_\mu\rangle = t_i^a(\mu), \quad (2.60)$$

together with usage of equation (2.57) and with some further rearrangements, we arrive at the equation for the  $T_1$  amplitudes:

$$(E - H_{\mu\mu}^{\text{eff}})t_i^a(\mu) = \langle (\Phi_\mu)_i^a | \hat{H}_N(\mu) e^{\hat{T}(\mu)} | \Phi_\mu \rangle_C.{}^7 \quad (2.61)$$

A notable difference with respect to the SRCC method is the emergence of the term  $(E - H_{\mu\mu}^{\text{eff}})t_i^a(\mu)$  on the left hand side, which yields a denominator shift. The other important difference is that for the MRCC approach, a set of equations has to be solved for every reference, whereas in the SRCC method we only deal with one set of equations.

Derivation of equation for the  $T_2$  amplitudes follows an analogous pattern and leads to the final expression:

$$(E - H_{\mu\mu}^{\text{eff}})\tau_{ij}^{ab} = \langle (\Phi_\mu)_{ij}^{ab} | \hat{H}_N(\mu) e^{\hat{T}(\mu)} | \Phi_\mu \rangle_C + \mathcal{P}(ij)\mathcal{P}(ab)t_i^a(\mu)\langle (\Phi_\mu)_j^b | \hat{H}_N(\mu) e^{\hat{T}(\mu)} | \Phi_\mu \rangle_C, \quad (2.62)$$

with  $\mathcal{P}(ij)$  being an antisymmetrization operator of indices  $i$  and  $j$  and

$$\tau_{ij}^{ab}(\mu) = \langle (\Phi_\mu)_{ij}^{ab} | e^{\hat{T}(\mu)} | \Phi_\mu \rangle = t_{ij}^{ab}(\mu) + t_i^a(\mu)t_j^b(\mu) - t_i^b(\mu)t_j^a(\mu) \quad (2.63)$$

For comparison, the  $T_2$  equation in the single reference approaches only comprises the first term from the right hand side of equation (2.62). Again, the left hand side of equation (2.62) is responsible for the denominator shift, which makes the method immune to intruder states.

Amplitude equations are iterative in the multi-reference case as well. The amplitudes are coupled with each other only through the total energy. As a result of that, the MR BWCC calculations can be split into  $M$  almost independent parts, which interact only when  $H^{\text{eff}}$  is diagonalized to obtain  $E$ .

MR BWCC is the generalisation of the SR CC theory. Accordingly, running a MR BWCC calculation with just one configuration reduces the whole formalism into the conventional SR CC case, as can be seen from Equations (2.61) and (2.62).

<sup>7</sup> $C$  denotes the so called connected term, taken from the terminology of the diagrammatic formalism of CC. It is beyond the scope of this thesis to go into detail about this formalism.

## Multireference Mukherjee Coupled Cluster Method

The multireference Mukherjee Coupled Cluster (MR-MkCC) method shares many of the features with the MR-BWCC theory. Therefore, this MkCC section will be written with reference to the BWCC approach.

In analogy with the BWCC method, a model space of  $M$  reference configurations is used. Linear combination of these  $M$  reference configurations, according to Equation (2.50), forms the basis of the model space. As in BWCC, the expansion coefficients,  $C_\mu$ , determine the weights of specific references.

The exact wave-function is obtained by action of the wave operator,  $\Omega$ , on the model space projection,  $\Phi$ ,

$$\Psi = \Omega\Phi. \quad (2.64)$$

The wave operator is considered in the Jeziorski-Monkhorst ansatz form, as shown in Equation (2.56).

As the next step, the *effective Hamiltonian operator* is defined as shown in Equation (2.53) to recover the exact energy,  $E$ , according to Equation (2.52).

Up to this point, the derivation of the MkCC approach was in complete analogy to the BWCC method. For the BWCC formalism, the next step was to utilise the Bloch equation, as shown in Equation (2.54). On the other hand, for Mukherjee coupled cluster method, the key step is to insert a resolution of identity constructed as

$$\begin{aligned} 1 &= e^{T(\mu)}e^{-T(\mu)} = e^{T(\mu)}(P + Q)e^{-T(\mu)} = \\ &= \sum_\nu e^{T(\mu)}|\nu\rangle\langle\nu|e^{-T(\mu)} + e^{T(\mu)}Qe^{-T(\mu)}, \end{aligned} \quad (2.65)$$

into the Schrödinger equation,

$$H_N\Omega\Phi = E\Omega\Phi. \quad (2.66)$$

After that, the summation indices  $\mu$  and  $\nu$  are interchanged in the first term, giving

$$\begin{aligned} \sum_\mu \left\{ \sum_\nu (e^{T(\nu)}|\Phi_\mu\rangle H_{\mu\nu}^{\text{eff}}C_\nu) + e^{T(\mu)}Qe^{-T(\mu)}H_Ne^{T(\mu)}|\Phi_\mu\rangle C_\mu \right. \\ \left. - Ee^{T(\mu)}|\Phi_\mu\rangle C_\mu \right\} = 0. \end{aligned} \quad (2.67)$$

Next, the so called *sufficiency conditions* are applied, i.e. that the contributions in the summation over  $\mu$  are all distinctly equal to zero.

The last step in acquiring the MkCC cluster equations is to premultiply Equation (2.67) by  $e^{-T(\mu)}$  and project with excited determinants,  $|\Phi_q\rangle$ , yielding

$$\langle \Phi_q | e^{-\hat{T}(\mu)} H_N e^{\hat{T}(\mu)} | \Phi_\mu \rangle C_\mu + \sum_{v \neq \mu} \langle \Phi_q | e^{-\hat{T}(\mu)} e^{\hat{T}(v)} | \Phi_\mu \rangle H_{\mu v}^{\text{eff}} C_v = 0. \quad (2.68)$$

Main difference in the structure of the MkCC equations when compared to the BWCC equations is the explicit presence of the expansion coefficients,  $C_\mu$  and  $C_v$ , in the MkCC equations, which are responsible for the coupling of the amplitudes. Cluster amplitudes of the excited determinants,  $T(v)$ , are also included in the MkCC equations through the  $e^{T(v)}$  terms, which is not the case for the BWCC equations.

## Multireference Explicitly Correlated Coupled Cluster Methods

The features of explicit correlation and multi-reference approaches can be merged to yield the multi-reference F12 coupled cluster method. Explicit correlation ensures a four orders of magnitude improved energy convergence with respect to the basis set. Multi-reference nature of the method assures correct treatment of systems with static correlation. Therefore, MR CC-F12 approaches represent one of the best performing alternatives in terms of accuracy and computational efficiency among the correlation energy methods.

Although the advantages of using the MR CC-F12 methods are clear, the whole formalism becomes quite complex. One of the more straightforward approaches is the generalisation of the Brillouin-Wigner multi-reference CC formalism with the F12 theory. Generalisation of the Mukherjee multi-reference CC approach with inclusion of the explicit correlation is also delivered in this section. The general features of theory presented in the preceding section remain valid for the MR CC-F12 approach as well. In the following, we will focus mainly on the differences which result from the introduction of the F12 theory into the formalism.

## The Brillouin-Wigner MR-F12 Approach

The multi-reference Brillouin-Wigner F12 coupled cluster (MR BWCC-F12) equations are derived analogously to the Brillouin-Wigner coupled cluster (MR BWCC) working equations. The first major difference is the replacement of the cluster operator  $\hat{T}(\mu)$  by  $\hat{S}(\mu)$ :

$$\hat{S}(\mu) = \hat{T}(\mu) + \hat{\mathcal{R}}(\mu), \quad (2.69)$$

implying that the wave operator of the MR BWCC-F12 method for the  $\omega$ -th electronic state becomes a combination of the MR BWCC and the CC-F12 ansatz:

$$\hat{\Omega} = \sum_{\mu=1}^M e^{\hat{T}(\mu) + \hat{\mathcal{R}}(\mu)} |\Phi_{\mu}\rangle \langle \Phi_{\mu}|. \quad (2.70)$$

$\hat{\mathcal{R}}(\mu)$  is the so called pseudo excitation operator with respect to the specific reference  $|\Phi_{\mu}\rangle$ . It is composed of two parts:

$$\hat{\mathcal{R}}(\mu) = \hat{\mathcal{R}}_1(\mu) + \hat{\mathcal{R}}_2(\mu) = c_k^i(\mu) \tilde{\mathcal{R}}_i^k(\mu) + \frac{1}{4} c_{kl}^{ij}(\mu) \tilde{\mathcal{R}}_{ij}^{kl}(\mu). \quad (2.71)$$

Our aim is to determine not only the amplitudes associated with  $\hat{T}$ , but also the amplitudes of the pseudo excitation operator,  $c_k^i(\mu)$  and  $c_{kl}^{ij}(\mu)$ . Using the STG factor with fixed theoretically determined amplitudes<sup>8</sup>,  $c_k^i(\mu)$  and  $c_{kl}^{ij}(\mu)$ , according to (2.49), instead of computing them, is a particularly potent approach that provides improved numerical stability and decreased sensitivity towards the RI description.

We now define Slater determinants excited with respect to  $|\Phi_{\mu}\rangle$  as  $|\Phi_{\vartheta}^{(\mu)}\rangle$ . While in the MR BWCC approach we focus on the projections onto  $|\Phi_{\vartheta}^{(\mu)}\rangle$ , in MR BWCC-F12 also the following projections are relevant in the derivation of the equations:

$$\langle \Phi_{\mu} | [\tilde{\mathcal{R}}_i^k(\mu)]^{\dagger} \quad (2.72)$$

and

$$\langle \Phi_{\mu} | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^{\dagger}. \quad (2.73)$$

Noting that

$$\langle \Phi_{\vartheta}^{(\mu)} | e^{\hat{\mathcal{R}}}(\mu) | \Phi_{\mu} \rangle = 0 \quad (2.74)$$

$$\langle \Phi_{\mu} | \hat{\mathcal{R}}^{\dagger}(\mu) e^{\hat{T}(\mu)} | \Phi_{\mu} \rangle = 0, \quad (2.75)$$

<sup>8</sup>Also known as the SP ansatz.

we start projecting on the configuration subspaces to get:

$$\begin{aligned}
(\mathcal{E} - H_{\mu\mu}^{\text{eff}}) \langle (\Phi_\mu)_i^a | e^{\hat{T}(\mu)} | \Phi_\mu \rangle &= \langle (\Phi_\mu)_i^a | [\hat{H}_N^{\text{ao}}(\mu) e^{\hat{T}(\mu)}]_C | \Phi_\mu \rangle + \\
&+ \langle (\Phi_\mu)_i^a | [\hat{H}_N^{\text{comp}}(\mu) e^{\hat{S}(\mu)}]_C | \Phi_\mu \rangle
\end{aligned} \tag{2.76}$$

$$\begin{aligned}
(\mathcal{E} - H_{\mu\mu}^{\text{eff}}) \langle (\Phi_\mu)_{ij}^{ab} | e^{\hat{T}(\mu)} | \Phi_\mu \rangle &= \langle (\Phi_\mu)_{ij}^{ab} | [\hat{H}_N^{\text{ao}}(\mu) e^{\hat{T}(\mu)}]_C | \Phi_\mu \rangle + \\
&+ \langle (\Phi_\mu)_{ij}^{ab} | [\hat{H}_N^{\text{ao}}(\mu) e^{\hat{T}(\mu)}]_{DC,L} | \Phi_\mu \rangle + \langle (\Phi_\mu)_{ij}^{ab} | [\hat{H}_N^{\text{comp}}(\mu) e^{\hat{S}(\mu)}]_C | \Phi_\mu \rangle \\
&+ \langle (\Phi_\mu)_{ij}^{ab} | [\hat{H}_N^{\text{comp}}(\mu) e^{\hat{S}(\mu)}]_{DC,L} | \Phi_\mu \rangle.
\end{aligned} \tag{2.77}$$

In the preceding, the Hamiltonian was decomposed into a computational basis set part ( $\hat{H}^{\text{ao}}$ ) and the orthogonal complement part ( $\hat{H}^{\text{comp}}$ ):

$$\hat{H}_N(\mu) = \hat{H}_N^{\text{ao}}(\mu) + \hat{H}_N^{\text{comp}}(\mu). \tag{2.78}$$

Now we perform projections onto the pseudo excitations space of F12 to obtain:

$$(\mathcal{E} - H_{\mu\mu}^{\text{eff}}) \langle \Phi_\mu | [\tilde{\mathcal{R}}_i^k(\mu)]^\dagger e^{\hat{\mathcal{R}}(\mu)} | \Phi_\mu \rangle = \langle \Phi_\mu | [\tilde{\mathcal{R}}_i^k(\mu)]^\dagger [\hat{H}_N^{\text{comp}}(\mu) e^{\hat{S}(\mu)}]_C | \Phi_\mu \rangle \tag{2.79}$$

$$\begin{aligned}
(\mathcal{E} - H_{\mu\mu}^{\text{eff}}) \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger e^{\hat{\mathcal{R}}(\mu)} | \Phi_\mu \rangle &= \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger [\hat{H}_N^{\text{comp}}(\mu) e^{\hat{S}(\mu)}]_C | \Phi_\mu \rangle \\
&+ \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger [\hat{H}_N^{\text{comp}}(\mu) e^{\hat{S}(\mu)}]_{DC,L} | \Phi_\mu \rangle.
\end{aligned} \tag{2.80}$$

Another major difference is in the expression for the effective Hamiltonian, which contains some extra terms:

$$\hat{H}_{\mu\nu}^{\text{eff}} = \langle \Phi_\mu | \hat{H} | \Phi_\mu \rangle \delta_{\mu\nu} + \langle \Phi_\mu | [\hat{H}_N^{\text{ao}}(\nu) e^{\hat{T}(\nu)}]_C | \Phi_\nu \rangle + \langle \Phi_\mu | [\hat{H}_N^{\text{comp}}(\nu) e^{\hat{S}(\nu)}]_C | \Phi_\nu \rangle. \tag{2.81}$$

Diagonal elements of  $\hat{H}_{\mu\mu}^{\text{eff}}$  represent the total energy for the reference state  $|\Phi_\mu\rangle$  with the involvement of both the  $\hat{T}(\mu)$  and the  $\hat{\mathcal{R}}(\mu)$  amplitudes. This is analogous to the MR BWCC formalism.

In order to better grasp the differences between the MR BWCC and the MR BWCC-F12 methods, it is useful to compare equations (2.76), (2.77), and (2.81) with (2.61), (2.62), and (2.57), respectively, to see which terms are identical for both approaches.

## The Mukherjee MR-F12 Approach

While deriving the Mk MRCCSD-F12 equations, we will make use of the equations already presented in the preceding sections in order to limit duplicating the information.

We start by defining the model space taken in the form of a linear combination of  $M$  reference configurations, as shown in Equation (2.50). The coefficients  $C_\mu$  are *a priori* unknown.

In order to obtain the exact wave-function, we act with the wave operator  $\Omega$  on the reference function,  $\Phi$ , according to Equation (2.64).

As a next step, we introduce the *effective Hamiltonian*,  $H^{\text{eff}}$ , as in Equation (2.53). The  $H^{\text{eff}}$  has the reference function  $\Phi$  as its eigenfunction and the exact energy,  $E$ , as the corresponding eigenvalue, as can be seen in Equation (2.52).

The wave operator is taken in the Jeziorski-Monkhorst ansatz form, which was used for the BW MRCCSD-F12 equations derivation, and is shown in Equation (2.70). We use the wave operator to formulate a matrix representation of the *effective Hamiltonian*

$$H_{\mu\nu}^{\text{eff}} = \langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle \delta_{\mu\nu} + \langle \Phi_\mu | e^{-\hat{S}(\nu)} \hat{H}_n(\nu) e^{\hat{S}(\nu)} | \Phi_\nu \rangle. \quad (2.82)$$

Diagonalisation of this matrix yields the expansion coefficients from Equation (2.50) as well as the energy of the specific state.

The internal cluster amplitudes, which correspondent to the excitations that transpose the reference configurations in between one another, are set to zero so that the intermediate normalisation of the wave-function is preserved. The rest of the amplitudes is determined by solving the cluster equations

$$\langle \Phi_q | e^{-\hat{S}(\mu)} \hat{H}_N(\mu) e^{\hat{S}(\mu)} | \Phi_\mu \rangle C_\mu + \sum_{\nu \neq \mu} \langle \Phi_q | e^{-\hat{S}(\mu)} e^{\hat{S}(\nu)} | \Phi_\mu \rangle H_{\mu\nu}^{\text{eff}} C_\nu = 0, \quad (2.83)$$

where  $\Phi_q$  is either an excited determinant from the Q-space (i.e. the configurations generated by  $\hat{T}(\mu)$ ) or a pseudo-excitation resulting from the action of  $\hat{\mathcal{R}}(\mu)$  on the reference determinant  $\Phi_\mu$ . These two types of projections lead to cluster equations for conventional amplitudes and the amplitudes associated with  $\hat{\mathcal{R}}(\mu)$ , respectively.

Two types of terms are present in Equation (2.83), the direct term, which is analogous to the single reference formalism and whose cost of computation is scaling linearly with increasing number of references, and the coupling terms that scale quadratically. In spite of that, the method preserves the linear scaling unless the model space is very large.

By comparing Equations (2.68) and (2.83), we note that the Mk MRCCSD-F12 equations are identical with the Mk MRCCSD equations, apart from the cluster operator,  $\hat{T}(\mu)$  being substituted with the excitation operator,  $\hat{S}(\mu)$ .

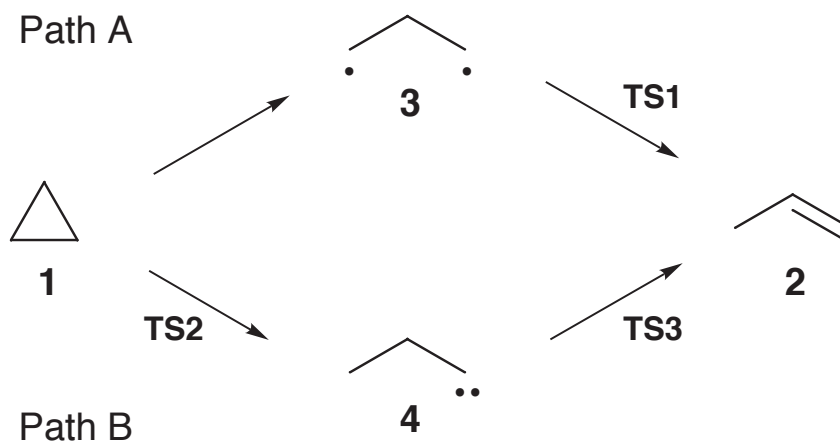
# Study of the Isomerisation of Cyclopropane to Propene

In spite of being one of the simplest organic reactions, the mechanism of isomerisation of cyclopropane (1) to propene (2) has proven to be a perplexing but nevertheless a fruitful research subject for both the computational and the experimental chemists.

The origins of the investigations can be traced to 1922, when Trautz and Winkler [60] have published kinetic data on the uncatalyzed thermal conversion of cyclopropane into propene. Their results, however, were questioned by several authors, among which were Chambers and Kistiakowsky [61], who came up with more accurate experiments. One of the highlights of their article was a suggestion that the reaction could follow a pathway through a diradical intermediate, the trimethylene species (3). Support for the trimethylene mechanism came with the seminal work of Rabinovitch, Schlag, and Wiberg [62], who reported that cis-trans isomerisation of cyclopropane competes with the structural isomerisation to propene. Numerous other experimental, computational, and thermochemical studies [63, 64, 65, 66, 67, 68] followed.

After the trimethylene mechanism became widely accepted, the focus of the scientists shifted into the energy characterisation of the reaction. Benson [69] reported a heat of formation of trimethylene based on the bond-additivity approach. His findings were later refined by Doering [70] and Borden *et al.*

Figure 3.1: The ring opening of cyclopropane can either pass through a trimethylene (3) intermediate (Path A) or propylidene (4) (Path B). In addition to these two mechanisms, cyclopropane is known to undergo a geometric isomerisation. Figure taken from ref. [59]



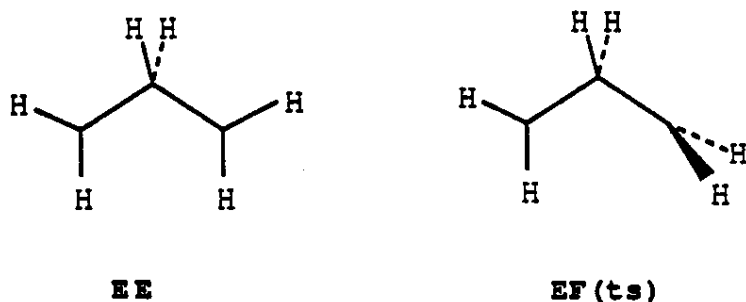
[71], although several major restrictions inherent in the methods used hindered further verification of the provided results [72]. The experimental studies made by Rabinovitch, Schleg, and Klein [63, 73, 74] reported activation energies of the gas-phase thermal isomerisation and the ring opening of cyclopropane to be 60-61 and 64-65 kcal mol<sup>-1</sup>, respectively. Getty *et al.* [75] and Yamaguchi *et al.* [76] stated that their *ab initio* calculations provided an activation energy of 61.6 kcal mol<sup>-1</sup>. More recent investigations [59, 77] have confirmed the activation energy of approximately 65 kcal mol<sup>-1</sup> for the conversion of cyclopropane into propene.

In spite of the general acclaim of the trimethylene mechanism, the diradical itself has never been observed experimentally. Validation of its existence came only in late 1994, when Pedersen, Herek, and Zewail [78] experimentally determined the lifetime of trimethylene to be 120 ± 20 fs. With this final piece of evidence in place, new developments in the investigation of the isomerisation became scarce. However, Bettinger *et al.* [59] proposed a new mechanism for the isomerisation of cyclopropane to propene. They considered propylidene (4), a diradical carbene, as the reactive intermediate, and they reported that such a pathway is energetically competitive with the traditional trimethylene mechanism. As far as we are concerned, there is no experimental evidence

supporting the path through (4).

The stereochemistry of the cyclopropane isomerisation was also thoroughly explored. In the pioneer studies [79, 80], Hoffman utilised extended Hückel theory and orbital symmetry arguments on the conformers of the trimethylene to identify the edge-to-edge form (EE; shown in Figure 3.2) as the reactive intermediate. He also argued that the preference for the EE structure is consistent with a conrotatory opening of the cyclopropane ring. The edge-to-face (EF; see Figure 3.2) form was found to be a transition state for the one-centre geometrical isomerisation of cyclopropane by Salem and co-workers [65, 81, 82]. They also reported the conrotatory optical isomerisation through the EE form is favoured to the one-centre geometrical isomerisation by way of EF, with a disrotatory path being even less competitive. Other studies which followed [75, 77, 83, 84] confirmed the kinetic and thermodynamic preference for the conrotatory ring-opening of cyclopropane.

Figure 3.2: The edge-to-edge (EE or "0,0") and the edge-to-face (EF or "0,90") forms of the trimethylene diradical.



In spite of all the efforts over the years, information about trimethylene coming from various sources is quite often contradictory. As an illustration, it has not yet been concluded if the ground state of trimethylene is singlet or triplet (see Figures 3.3 and 3.4). Goldberg and Dougherty [85] reported dependence of the singlet-triplet gap on the C-C-C valence angle at RHF and MCSCF levels of theory. However, Skancke *et al.* [86] concluded that the triplet is the ground state by 0.7 kcal/mol in their CASPT2N(2,2) calculations. Most of the computational analyses decided to perform the calculations on the singlet state, as is the case in our study as well.

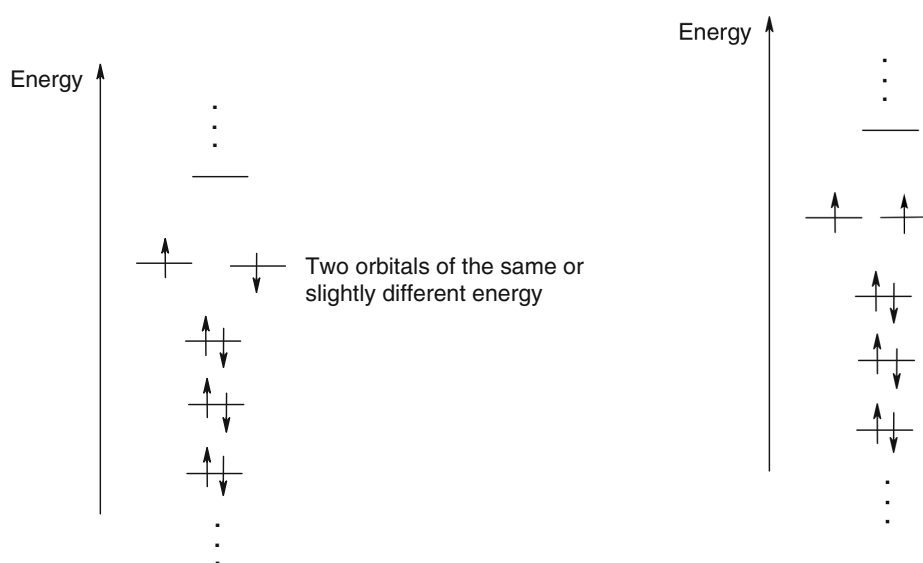


Figure 3.3: A singlet state of a diradical - two unpaired electrons with opposite spin. Taken from ref. [87].

Figure 3.4: A triplet diradical - two unpaired electrons with the same spin.

The isomerisation of cyclopropane to propene was studied from all kinds of perspectives, both experimentally and theoretically. The whole plethora of investigations devoted to this reaction shows us just how intriguing even the simplest reactions can be. Our motivation to study this reaction partially comes from the research done on more complicated systems [88, 86, 89, 90, 91], which involve the trimethylene diradical intermediates, where the knowledge derived from this simpler case is utilised.

One of the other main reasons why we chose to perform our calculations on this isomerisation reaction in particular is the multi-reference nature of the trimethylene diradical. Also, its significance as a reactive intermediate in quite some organic reactions is an ongoing subject [87, 92]. The foremost aim of our study is to provide high-precision computational results that will replace some of the outdated results of previous computational studies.

## Computational Details

The aim of our computations was to compare the performance of the multi-reference methods without and with explicit correlation, MRBWCCSD(T), MkCCSD(T), MRBWCCSD(T)-F12, MkCCSD(T)-F12, with the conventional methods such as CCSD(T) and some other approaches reported in literature.

We performed calculations on three species of the cyclopropane isomerisation to propene. Two of them, trimethylene and propylidene, are of multi-determinant nature and therefore the multi-reference methods employed are used to their full potential. The last structure adopted was the cyclopropane itself, so that we would be able to judge the quality of our results based on comparison with other computational studies. We focus on the trimethylene diradical due to its multi-reference nature.

Geometry optimisation of the trimethylene and propylidene was performed in the MOLPRO software package [93], using the CASPT2(6,6) method without symmetry, and the cc-pVQZ basis set. The equilibrium structure of cyclopropane was taken from an article by Gauss, Cremer, and Stanton [94], who calculated its geometry at the CCSD(T)/cc-pVQZ level. Appendix A contains the optimised geometry parameters.

Vibrational analysis was performed on both trimethylene and cyclopropane and it confirmed that both are indeed minima since all the vibrational frequencies were real.

For all single-point energy calculations, the three lowest lying orbitals (i.e. the 1s orbitals on carbon atoms) were kept frozen for cyclopropane, trimethylene, and propylidene.

The single reference CCSD(T) calculations were performed with the parallelised Nwchem program, [95] employing the Dunning correlation consistent polarised basis sets cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z [96]. For all the other methods, calculations in the cc-pV5Z basis were omitted due to prohibitive computational cost.

The BW MRCCSD(T) as well as the explicitly correlated CCSD(T)-F12, BW MRCCSD(T)-F12, and MkCCSD(T)-F12 computations were run in the CCR12-OS program developed by Noga's and our group [97]. For the Brillouin-Wigner

multi-reference calculations, the a posteriori correction was applied. Fixed amplitudes were employed in all explicit correlation calculations due to the size of the basis sets used.

Both the Aces II software [98] and the CCR12-OS were utilised to calculate the MkCCSD(T) energies. Equivalence of these two approaches was checked prior to commencing the calculations. The energy differences between these two packages were less than  $10^{-6}$  a.u. Such a difference can already be attributed to numerical noise, when default thresholds and convergence criteria are employed.

The HF energies were extrapolated to a complete basis set, according to the following scheme:

$$E_n^{\text{HF}} = E_\infty^{\text{HF}} + a \cdot \exp(-bn), \quad (3.1)$$

where  $n$  is the basis set cardinal number.

The correlation energies were extrapolated at the conventional level according to the formula:

$$E_n^{\text{corr}} = E_\infty^{\text{corr}} + an^{-3}, \quad (3.2)$$

where  $n$  is the cardinal number of the basis set used.

## Results and Discussion

This section is divided into four parts. First, we present results from calculations done on the trimethylene intermediate. Subsequently, results for propylidene and cyclopropane follow. Finally, we investigate the energy differences between these three species and compare them with the literature results.

### Trimethylene

The trimethylene subsection is divided into smaller parts. We start by reporting the results of the single reference calculations, CCSD(T) and CCSD(T)-F12, and their performance with respect to each other. Next, both the BWCC/BWCC-F12 and MkCC/MkCC-F12 sets of multi-reference results are shown and compared. Finally, the conventional results are compared with each other, followed by the comparison of the explicitly correlated calculations.

#### Single reference Calculations

Table 3.1 summarises the results of the conventional single reference calculations. The first column of Table 3.1 contains the basis sets used, the second and fourth columns contain the CCSD and CCSD(T) energies, respectively, and in the third and fifth columns the differences in energies for two successive basis sets are shown. Description of Tables 3.2, 3.4, and 3.5 is analogous to this table.

Let us look at the trend in the convergence of the total energy. There is a difference of 71.09 and 76.08 kcal/mol in between the DZ and the TZ basis sets for CCSD and CCSD(T), respectively. Increased basis set size yields an increase in accuracy as more space is provided for the electrons to move around in the orbitals so their correlation is better described. For instance, the differences between the QZ and the 5Z basis sets are only 5.92 and 6.26 kcal/mol for the CCSD and CCSD(T), respectively. Such a small difference also means that we are already quite close to the complete basis set (CBS) limit.

In an ideal case scenario, we would like the differences of energies with respect to the basis set size to diminish completely. In such a case, we would say we have reached the CBS limit. However, the amount of resources that would have to be used to reach the CBS limit accuracy is insurmountable, due to  $n^{-3}$  scaling. Instead, a different technique is used to obtain an educated guess of the CBS limit - basis set extrapolation. For these conventional calculations, we

Table 3.1: Total CCSD and CCSD(T) energies (in Hartrees) and energy differences,  $\Delta E$  (in kcal/mol), between two consecutive basis sets within the same method.

Basis set	CCSD	$\Delta E$	CCSD(T)	$\Delta E$
cc-pVDZ	-117.4006270	–	-117.4443947	–
cc-pVTZ	-117.5139220	71.09	-117.5656339	76.08
cc-pVQZ	-117.5454594	19.79	-117.5989118	20.88
cc-pV5Z	-117.5548911	5.92	-117.6088864	6.26
CBS limit	-117.5648344	6.24	-117.6194893	6.65

used the TZ-5Z basis sets for the energy extrapolation, because results provided by DZ basis are frequently unreliable. One can see from Table 3.1 that the CBS limit value of -117.5648344 is still 6.24 kcal/mol lower in energy than the 5Z result. This shows us that even in the 5Z basis set, the energy is still not sufficiently converged. Slow convergence of the CCSD/CCSD(T) total energy with respect to the basis set is a generally known fact.

By inspecting the data shown in Tables 3.1 and 3.2, we can compare the performance of the conventional CCSD/CCSD(T) methods with their F12 counterparts in terms of total energy convergence with respect to the basis set size. If we look at the energy difference between the DZ and the TZ basis sets, we see values 19.02 and 26.76 kcal/mol for the CCSD-F12/CCSD(T)-F12, respectively, and 71.09 and 76.08 kcal/mol for the CCSD/CCSD(T) approaches. Comparing these values as well as the energy differences between the other basis sets used tells us that the total energy convergence is rapidly speeded up by employing explicit correlation.

Another thing to note is that the convergence of the CCSD total energy towards the CBS limit is faster than the convergence of the CCSD(T) total energy.

Table 3.3 compares the performance of the conventional (CCSD/CCSD(T)) and explicitly correlated approaches with respect to each other in terms of absolute energy differences between these methods within the same basis sets. We see the highest difference at the DZ basis set level, with decreasing energy differences as we employ basis sets of higher quality. We also note that the total energies calculated with explicit correlation in a basis set of cardinal number

Table 3.2: Total CCSD-F12 and CCSD(T)-F12 energies (in Hartrees) and energy differences,  $\Delta E$  (in kcal/mol), between two consecutive basis sets within the same method.

Basis set	CCSD-F12	$\Delta E$	CCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.5138231	–	-117.5502851	–
cc-pVTZ	-117.5441385	19.02	-117.5929229	26.76
cc-pVQZ	-117.5561974	7.57	-117.6083633	9.69
CBS limit <sup>a</sup>	-117.5648344	5.42	-117.6194893	6.98

<sup>a</sup>CBS limit was obtained from conventional calculations.

Table 3.3: Total CCSD/CCSD-F12 and CCSD(T)/CCSD(T)-F12 energies (in Hartrees) and the energy differences,  $\Delta E$  (in kcal/mol), in between these methods within the same cc-pVnZ basis set.

Basis set	CCSD	CCSD-F12	$\Delta E$
cc-pVDZ	-117.4006270	-117.5138231	66.45
cc-pVTZ	-117.5139220	-117.5441385	17.12
cc-pVQZ	-117.5454594	-117.5561974	5.93
cc-pV5Z	-117.5548911	–	–
Basis set	CCSD(T)	CCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.4443947	-117.5502851	71.03
cc-pVTZ	-117.5656339	-117.5929229	18.96
cc-pVQZ	-117.5989118	-117.6083633	6.74
cc-pV5Z	-117.6088864	–	–

Table 3.4: Total BWCCSD/MkCCSD and BWCCSD(T)/MkCCSD(T) energies (in Hartrees) for the cc-pVnZ basis sets and relative energies,  $\Delta E$  (in kcal/mol), in between two consecutive basis sets within the same method.

Basis set	BWCCSD	$\Delta E$	BWCCSD(T)	$\Delta E$
cc-pVDZ	-117.4302868	–	-117.4533736	–
cc-pVTZ	-117.5464093	72.87	-117.5792889	79.01
cc-pVQZ	-117.5782498	19.98	-117.6137433	21.62
BW CBS limit	-117.5991719	13.13	-117.6365728	14.33
Basis set	MkCCSD	$\Delta E$	MkCCSD(T)	$\Delta E$
cc-pVDZ	-117.4249388	–	-117.4466604	–
cc-pVTZ	-117.5403292	72.41	-117.5714771	78.32
cc-pVQZ	-117.5718141	19.76	-117.6054673	21.33
Mk CBS limit	-117.5924767	12.97	-117.6279581	14.11

$n$  almost reach the accuracy of the conventional total energies computed in an  $(n + 1)$  basis set. Due to the  $\mathcal{O}(n^4)$  scaling of the CCSD/CCSD(T) methods with respect to the basis set size, use of explicit correlation provides significant savings in computational times.

### Multi-reference Calculations

Table 3.4 contains data collected from the conventional BWCCSD(T) and MkCCSD(T) calculations. In spite of recovering on average 19.86/7.84 kcal/mol more correlation energy than the CCSD/CCSD(T) calculations, respectively, the convergence towards the CBS limit remains slow even for the Brillouin-Wigner multi-reference calculations.

Comparing the BWCCSD/BWCCSD(T) energy differences between consecutive basis sets with their conventional single reference counterparts, we can see that the trend in the total energy convergence with respect to the basis set size has not changed. The energy differences between the DZ and the TZ basis sets are 72.87 and 79.01 kcal/mol for the BWCCSD and BWCCSD(T), respectively.

The energy differences between two consecutive basis sets for the Mukher-

Table 3.5: Total BWCCSD-F12/BWCCSD(T)-F12 and MkCCSD-F12/MkCCSD(T)-F12 energies (in Hartrees) and the energy differences,  $\Delta E$  (in kcal/mol), between two consecutive basis sets within the same method.

Basis set	BWCCSD-F12	$\Delta E$	BWCCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.5483797	–	-117.5695180	–
cc-pVTZ	-117.5780379	18.61	-117.6098772	25.33
cc-pVQZ	-117.5895120	7.20	-117.6245109	9.18
BW CBS limit	-117.5991719	6.06	-117.6365728	7.57
Basis set	MkCCSD-F12	$\Delta E$	MkCCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.5429243	–	-117.5628254	–
cc-pVTZ	-117.5719222	18.20	-117.6020902	24.64
cc-pVQZ	-117.5830650	6.99	-117.6162551	8.89
Mk CBS limit <sup>a</sup>	-117.5924767	5.91	-117.6279581	7.34

<sup>a</sup>Both BW CBS limit and Mk CBS limit computed at the conventional level.

jee’s multi-reference computations exhibit a minor variation as compared to the BWCCSD/BWCCSD(T) energy differences, on the order of magnitude of tenth of a kcal/mol. In other words, the total energy convergence trend maintains the same pattern in the conventional Mukherjee’s computations that was observed in the conventional Brillouin-Wigner calculations.

Data from BWCCSD(T)-F12 and MkCCSD(T)-F12 calculations are presented in Table 3.5. The difference between these explicitly correlated results and the conventional results is in the characteristic boost in total energy convergence provided by employing explicit correlation.

One other important remark is that the triples perturbative correction is implemented only at the conventional level, thus even for the F12 computations the triples correction is only performed at a conventional level.

Data from Table 3.6, enable us to compare the performance of the conven-

Table 3.6: Total Brillouin-Wigner and Mukherjee energies (in Hartrees) calculated both at the conventional and the F12 level and the energy differences,  $\Delta E$  (in kcal/mol), between the conventional and the F12 calculations within the same basis set.

Basis set	BWCCSD	BWCCSD-F12	$\Delta E$
cc-pVDZ	-117.4302868	-117.5483797	74.10
cc-pVTZ	-117.5464093	-117.5780379	19.85
cc-pVQZ	-117.5782498	-117.5895120	7.07
Basis set	BWCCSD(T)	BWCCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.4533736	-117.5695180	72.88
cc-pVTZ	-117.5792889	-117.6098772	19.19
cc-pVQZ	-117.6137433	-117.6245109	6.76
Basis set	MkCCSD	MkCCSD-F12	$\Delta E$
cc-pVDZ	-117.4249388	-117.5429243	74.04
cc-pVTZ	-117.5403292	-117.5719222	19.82
cc-pVQZ	-117.5718141	-117.5830650	7.06
Basis set	MkCCSD(T)	MkCCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.4466604	-117.5628254	72.89
cc-pVTZ	-117.5714771	-117.6020902	19.21
cc-pVQZ	-117.6054673	-117.6162551	6.77

tional Brillouin-Wigner and Mukherjee approaches with their explicitly correlated variants relative to each other.

The difference in the amount of correlation energy extracted by both the BWCCSD and MkCCSD methods with respect to their F12 counterparts diminishes as we use basis sets of better quality, from 74.10/74.04 kcal/mol for the DZ basis set to 7.07/7.06 kcal/mol for the QZ basis, respectively. Same trend is observed at the BWCCSD(T) and MkCCSD(T) level, when we compare the conventional and the F12 approaches with each other.

## Comparison of Conventional and Explicitly Correlated Results.

Results from all conventional calculations are shown in Figure 3.5. We can see that the energy gap between the single reference results (red line) and the BWCC (blue line) and the MkCC (green line) results is significant: 21.29/17.52 kcal/mol on average at the CCSD level, respectively, and 10.95/6.19 kcal/mol on average with the perturbative triples included, respectively. The differences are lower at the CCSD(T) level due to the better description of the static correlation provided by the triples excitations.

Also note that the perturbative triples correction is sufficient to describe a considerable part of static correlation and therefore the single reference, BWCC, and MkCC approaches are much closely packed together at the CCSD(T) level than at the CCSD level. In other words, we gain a substantial improvement in energy provided by the multi-reference treatment as opposed to the single reference calculations at the CCSD level, but not so significant enhancement at the CCSD(T) level.

The green and cyan MkCC lines and the blue and pink BWCC lines in Figure 3.5 are closely copying each other, with an average energy difference of 3.74 kcal/mol at the CCSD level and 4.77 kcal/mol with perturbative triples included, i.e. the energy differences between the MkCC and the BWCC approaches are almost constant with respect to the basis set size.

Results of all our explicitly correlated calculations are presented in Figure 3.6. There are two main consequences resulting from employing the explicit correlation. Firstly, rapid total energy convergence as opposed to the conventional methods, which can be seen by comparing Figures 3.5 and 3.6. The slopes of the lines at the F12 level are mild when compared with the slopes of the lines at the conventional level, which are quite steep. Also, all F12 results are located below the  $-117.5 E_h$ , whereas the conventional results are spread around from  $-117.4 E_h$ . Secondly, the separation between the single reference, the BWCC, and the MkCC energies increases when explicit correlation is employed both at the CCSD and the CCSD(T) levels.

Figure 3.5: Convergence of the total CCSD/BWCCSD/MkCCSD and CCSD(T)/BWCCSD(T)/MkCCSD(T) energies with respect to the basis set size.

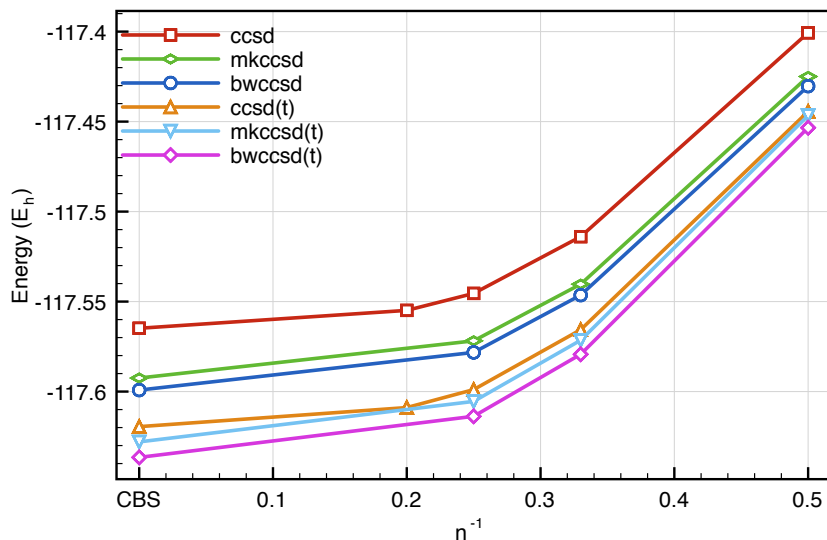
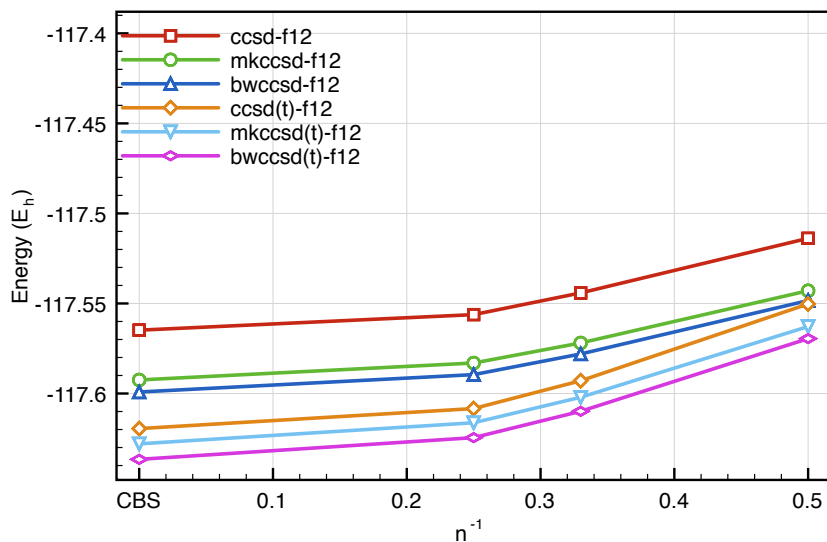


Figure 3.6: Convergence of the total explicitly correlated CCSD/BWCCSD/ MkCCSD and CCSD(T)/BWCCSD(T)/MkCCSD(T) energies with respect to the basis set size. CBS limits taken from the conventional CCSD(T)/ BWCCSD(T)/MkCCSD(T) methods.



## Propylidene

The propylidene section is divided into smaller parts analogously to the trimethylene section. We start by reporting the results of the single reference calculations, CCSD(T) and CCSD(T)-F12, and their comparison. Next, both the BWCC and BWCC-F12 multi-reference and the MkCC and the MkCC-F12 results are shown and contrasted. In the last subsection, the conventional single reference, BWCC, and MkCC results are presented together and the BWCC-F12 and the MkCC-F12 calculations outcomes are confronted with the single reference F12 results.

Like trimethylene, propylidene has a multi-reference character as well, but it is much less pronounced. For trimethylene, the weights of the two most important references are very close to each other, with a 63:37 ratio, whereas for propylidene the ratio with which the two most important references contribute to the correlation energy is 98:2. Many of the trends described for the trimethylene calculations are the same for the propylidene case, while only a few differ. The whole propylidene section is thus presented with references to the trimethylene passage.

### Single reference Calculations

Results from single reference CCSD/CCSD(T) calculations are presented in Table 3.7. First column of Table 3.7 shows the basis set used, second and fourth columns contain the absolute energies in Hartrees and third and fifth columns comprise of the energy differences between two consecutive basis sets (i.e. DZ - TZ and so on). Description of Tables 3.8, 3.10, and 3.11 is analogous to this table.

The convergence trend for CCSD and CCSD(T) calculations, which can be seen in Table 3.7, follows the trend observed for trimethylene single reference calculations. The energy differences between the basis sets only differ by approximately 0.1-2 kcal/mol when comparing propylidene results with trimethylene results. For example, CCSD/QZ and CCSD/5Z  $\Delta E$  is 5.92 kcal/mol for trimethylene and 6.04 kcal/mol for propylidene.

We also note that due to the overall energy convergence of couple cluster single reference calculations being very slow, we need to perform calculations in QZ or higher basis set levels to achieve results of desirable quality. It is true for both CCSD and CCSD(T) computations.

Table 3.7: Total CCSD and CCSD(T) energies (in Hartrees) and energy differences,  $\Delta E$  (in kcal/mol), between two consecutive basis sets within the same method.

Basis set	CCSD	$\Delta E$	CCSD(T)	$\Delta E$
cc-pVDZ	-117.4175776	–	-117.4304229	–
cc-pVTZ	-117.5343556	73.28	-117.5545811	77.91
cc-pVQZ	-117.5667424	20.32	-117.5888711	21.52
cc-pV5Z	-117.5763723	6.04	-117.5991361	6.44
CBS limit	-117.5863874	6.28	-117.6098674	6.73

Table 3.8: Total CCSD-F12 and CCSD(T)-F12 energies (in Hartrees) and energy differences,  $\Delta E$  (in kcal/mol), between two consecutive basis sets within the same method.

Basis set	CCSD-F12	$\Delta E$	CCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.5364420	–	-117.5479799	–
cc-pVTZ	-117.5660505	18.58	-117.5855026	23.55
cc-pVQZ	-117.5780179	7.51	-117.5997719	8.95
CBS limit <sup>a</sup>	-117.5863874	5.25	-117.6098674	6.34

<sup>a</sup>CBS limit was computed at the conventional level.

Let us now have a look at the explicitly correlated single reference calculations, which are presented in Table 3.8. When comparing the energy differences between two successive basis sets,  $\Delta E$ , obtained for trimethylene and propylidene, there are only small discrepancies within 2 kcal/mol.

By inspecting Table 3.8, one can observe how accelerated the convergence of the total energy with respect to the basis set size is when explicit correlation is employed. The energy difference between the DZ and the TZ basis sets for the CCSD-F12/CCSD(T)-F12 approaches is 18.58/23.55 kcal/mol, respectively, which is very close to the energy difference of 20.32/21.52 kcal/mol between the TZ and the QZ basis sets for the conventional CCSD/CCSD(T) methods, respectively. The CCSD-F12/TZ energy is well below the CCSD/TZ energy and it also surpasses the CCSD/QZ result.

Table 3.9: Total CCSD and CCSD-F12 energies and the differences of energies  $\Delta E$  of these two methods for the cc-pVNZ basis sets.

Basis set	CCSD	CCSD-F12	$\Delta E$
cc-pVDZ	-117.4175776	-117.5364420	73.77
cc-pVTZ	-117.5343556	-117.5660505	2.41
cc-pVQZ	-117.5667424	-117.5780179	0.23
cc-pV5Z	-117.5763723	–	–
Basis set	CCSD(T)	CCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.4304229	-117.5479799	74.59
cc-pVTZ	-117.5545811	-117.5855026	2.47
cc-pVQZ	-117.5888711	-117.5997719	0.24
cc-pV5Z	-117.5991361	–	–

Table 3.9 contains the differences in energies between the conventional and the F12 approaches. The most important thing to note is that employing explicit correlation speeds up the convergence of the total energy as if we used a basis set of higher quality at the conventional level. For instance, both the CCSD-F12/QZ and the CCSD(T)-F12/QZ energies are lower than the CCSD/5Z and CCSD(T)/5Z results by 0.4 and 1.03 kcal/mol, respectively. One can also see that the improvement at the DZ level is enormous.

Comparing the single reference results obtained for propylidene with trimethylene results, which are summarised in Tables 3.9 and 3.3, respectively, we observe that employing explicit correlation has larger effect on trimethylene results in recovering more correlation energy than in the case of propylidene.

### Multi-reference Calculations

Conventional multi-reference Brillouin-Wigner and Mukherjee’s results are presented in Table 3.10. The trend of the energy convergence of the BWCCSD/BW-CCSD(T) and MkCCSD/MkCCSD(T) methods is once more almost identical to the trend of the same methods for the trimethylene diradical. The discrepancies in  $\Delta E$  are not higher than 1 kcal/mol.

The BWCC-F12 and MkCC-F12 results are presented in Table 3.11. The con-

Table 3.10: Total BWCCSD/BWCCSD(T) and MkCCSD/MkCCSD(T) energies (in Hartrees) and energy differences,  $\Delta E$  (in kcal/mol) between two consecutive basis sets within the same approach.

Basis set	BWCCSD	$\Delta E$	BWCCSD(T)	$\Delta E$
cc-pVDZ	-117.4192800	–	-117.4313932	–
cc-pVTZ	-117.5363521	73.46	-117.5557591	78.04
cc-pVQZ	-117.5688525	20.39	-117.5901563	21.58
BW CBS limit	-117.5895559	12.99	-117.6122439	13.86
Basis set	MkCCSD	$\Delta E$	MkCCSD(T)	$\Delta E$
cc-pVDZ	-117.4187602	–	-117.4308567	–
cc-pVTZ	-117.5356299	73.34	-117.5550226	77.92
cc-pVQZ	-117.5679884	20.31	-117.5892857	21.50
Mk CBS limit <sup>a</sup>	-117.5885883	12.93	-117.6112753	13.80

<sup>a</sup>Both BW CBS limit and Mk CBS limit were calculated at the conventional level.

vergence of total energy is speeded up due to the explicit correlation treatment. The differences in energies between successive basis sets,  $\Delta E$ , follow the same trend that was encountered at the trimethylene system.

Table 3.12 contains the data collected from BWCC-F12 and MkCC-F12 calculations and their conventional equivalents. Similarly to the trimethylene case, explicitly correlated results in a basis set of a cardinal number  $n$  are approximately of the quality of conventional results in an  $(n + 1)$  basis set, in terms of total energies.

### Comparison of Conventional and Explicitly Correlated Results

All our results calculated at the conventional level are presented together in Figure 3.7 so that their performance relative to each other can be compared. If we look at Figure 3.7, it can be observed that the red, green, and pink lines, which represent the single reference, BWCC, and MkCC results, respectively, are directly on top of each other, with a slight notable difference in path of the red CCSD line. With the perturbative triples correction included, the lines representing the methods at this level are almost perfectly aligned. To be more

Table 3.11: Total BWCCSD-F12/BWCCSD(T)-F12 and MkCCSD-F12/MkCCSD(T)-F12 energies (in Hartrees) and the energy differences,  $\Delta E$ , between two successive basis sets within the same approach.

Basis set	BWCCSD-F12	$\Delta E$	BWCCSD(T)- F12	$\Delta E$
cc-pVDZ	-117.5384919	–	-117.5494296	–
cc-pVTZ	-117.5681686	18.62	-117.5868593	23.49
cc-pVQZ	-117.5801712	7.53	-117.6011257	8.95
BW CBS limit	-117.5895559	5.89	-117.6122439	6.98
Basis set	MkCCSD-F12	$\Delta E$	MkCCSD(T)- F12	$\Delta E$
cc-pVDZ	-117.5379441	–	-117.5488678	–
cc-pVTZ	-117.5674392	18.51	-117.5861173	23.37
cc-pVQZ	-117.5793073	7.45	-117.6002572	8.87
Mk CBS limit <sup>a</sup>	-117.5885883	5.82	-117.6112753	6.91

<sup>a</sup>Both BW CBS limit and Mk CBS limit were obtained from conventional calculations.

specific, the differences in the single reference results and the BWCC and the MkCC results range from 0.7 kcal/mol to 1.99 kcal/mol at the CCSD level, and from 0.27 kcal/mol to 1.49 kcal/mol at the perturbative triples level.

CBS limits were all calculated from the conventional calculations data. Results from TZ, QZ, and 5Z were used for single reference CBS limit extrapolation, whereas TZ, and QZ basis sets were used for extrapolation in BWCC and MkCC formalisms.

Let us compare the TZ basis results obtained at the CCSD level for propylidene and trimethylene. For propylidene, the difference between the single reference and the BWCC results was 1.25 kcal/mol, and the single reference and MkCC results difference was 0.80 kcal/mol. If we look at the same differences calculated for the trimethylene system, we note they are 20.39, 16.57 kcal/mol, respectively. It seems that for propylidene, the CCSD calculations are already sufficient for correct description of the system. Use of BWCC and MkCC multi-reference approaches does not provide a significant improvement

Table 3.12: Total Brillouin-Wigner and Mukherjee’s energies (in Hartrees) computed both at the conventional and the F12 levels and the energy differences,  $\Delta E$  (in kcal/mol), between the conventional and the F12 calculations results, for the cc-pVnZ basis sets.

Basis set	BWCCSD	BWCCSD-F12	$\Delta E$
cc-pVDZ	-117.4192800	-117.5384919	74.81
cc-pVTZ	-117.5363521	-117.5681686	19.97
cc-pVQZ	-117.5688525	-117.5801712	7.10
Basis set	BWCCSD(T)	BWCCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.4313932	-117.5494296	74.07
cc-pVTZ	-117.5557591	-117.5868593	19.52
cc-pVQZ	-117.5901563	-117.6011257	6.88
Basis set	MkCCSD	MkCCSD-F12	$\Delta E$
cc-pVDZ	-117.4187602	-117.5379441	74.79
cc-pVTZ	-117.5356299	-117.5674392	19.96
cc-pVQZ	-117.5679884	-117.5793073	7.10
Basis set	MkCCSD(T)	MkCCSD(T)-F12	$\Delta E$
cc-pVDZ	-117.4308567	-117.5488678	74.05
cc-pVTZ	-117.5550226	-117.5861173	19.51
cc-pVQZ	-117.5892857	-117.6002572	6.88

relative to the single reference CCSD results. On the other hand, the single reference calculations values obtained for trimethylene are quite far in energy when compared with the multi-reference approaches values. Therefore, in the case of trimethylene, single reference calculations at the CCSD level are not satisfactory and multi-reference approaches need to be used to account for the static correlation which appears due to the multi-reference nature of trimethylene.

When the perturbative triples are included in the calculations, the differences between the single reference approach and the BWCC and MkCC multi-reference approaches at the TZ basis set are reduced to 8.57 and 3.67 kcal/mol,

respectively, for trimethylene, and to 0.74 and 0.28 kcal/mol, respectively, for propylidene. This decrease in the energy differences is due to the perturbative triples excitations correction, which accounts for considerable part of the static correlation.

At the CBS limit level, the differences between the single reference and the BWCC and the MkCC approaches are the highest: 1.99 and 1.38 kcal/mol at the CCSD level and 1.49 and 0.88 kcal/mol with perturbative triples included. Even though these CBS limit energy differences are higher than the energy differences in the other basis sets, the variation in the basis sets used for extrapolation at the single reference and the BWCC and the MkCC levels of theory might be the reason for such a disparity.

Let us now have a look at the explicitly correlated results, which are summarised in Figure 3.8. Comparing Figures 3.7 and 3.8, we observe a huge difference in the energies calculated at the conventional level with respect to the results acquired when explicit correlation was employed. The F12 results are much closely packed together, with the calculations at the CCSD/DZ level located around the  $-117.54 E_h$  value and the CCSD(T)/QZ results being at  $-117.6 E_h$ .

With the explicit correlation included, the differences between the single reference and multi-reference total energies is insignificant, being approximately 0.1 kcal/mol. These minute differences tell us that with the CCSD-F12/CCSD(T)-F12 level of theory and TZ/QZ basis sets employed, the single reference and the multi-reference BWCC and MkCC approaches begin to perform equivalently well for propylidene.

Figure 3.7: Convergence of the total CCSD/BWCCSD/MkCCSD and CCSD(T)/BWCCSD(T)/MkCCSD(T) energies with respect to the basis set size.

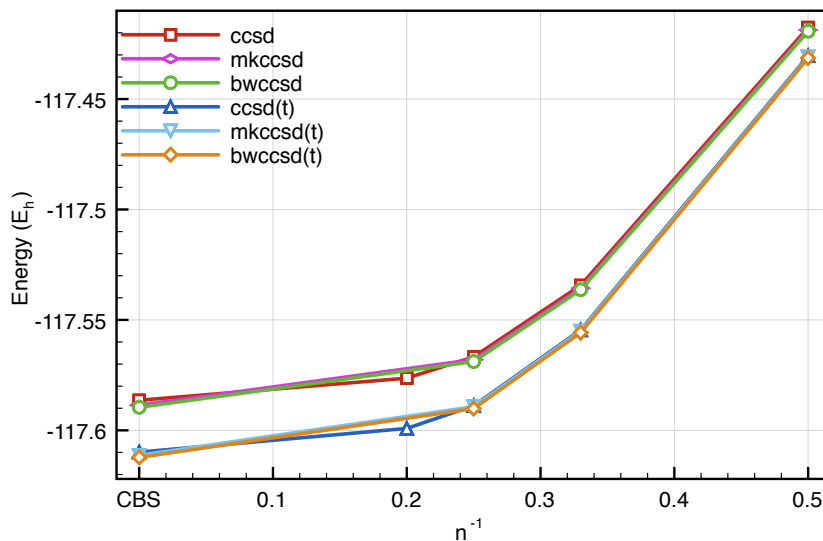
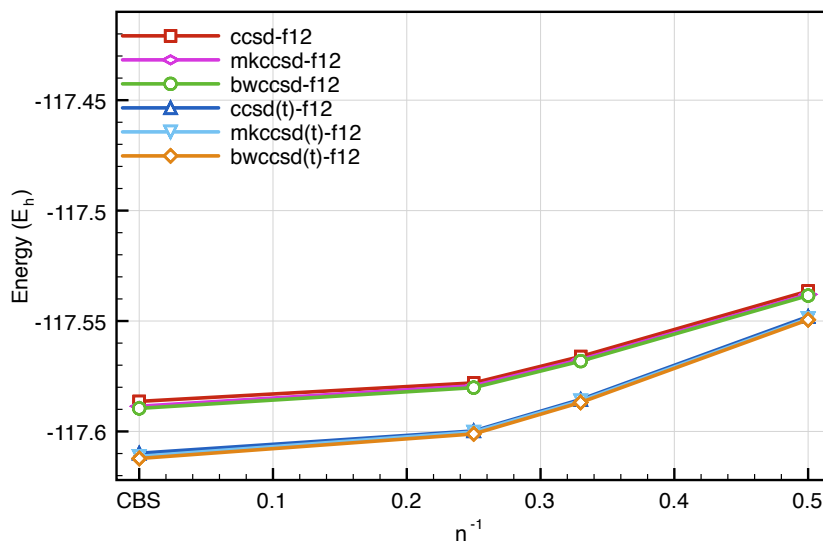


Figure 3.8: Convergence of the total explicitly correlated CCSD/BWCCSD/ MkCCSD and CCSD(T)/BWCCSD(T)/MkCCSD(T) energies with respect to the basis set size. CBS limits taken from the conventional CCSD(T) /BWCCSD(T)/MkCCSD(T) methods.



## Cyclopropane

This section, which is devoted to cyclopropane, is organised differently than the two preceding sections about trimethylene and propylidene. This simplified organisation is chosen because cyclopropane is not a multi-reference system and therefore is not in the focus in this thesis. However, all cyclopropane results are crucial for calculating the energy profile of the reaction and therefore also serve us in comparing our results with literature results.

All the conventional and explicitly correlated results are summarised Table 3.13. The convergence trends are essentially the same for cyclopropane as they were for the trimethylene and propylidene systems, so they will not be discussed.

We can explore Table 3.13 to compare the total energies acquired with the conventional calculations. We observe that the energy differences between the single reference formalism and the BWCC and the MkCC approaches at both the CCSD and the CCSD(T) levels are virtually non-existent, being at most 0.02 kcal/mol. Therefore, the performance of all three methods we used is the same for a single reference system such as cyclopropane.

The only discrepancy occurs for the CBS limits. This is again due to the way the CBS extrapolation was executed, using TZ-5Z basis sets for single reference extrapolation and TZ and QZ basis sets for both the BWCC and the MkCC CBS extrapolations.

If we observe the data acquired from the F12 calculations, which are summarised in the second part of Table 3.13, the single reference and multi-reference total energies calculated at the CCSD-F12/CCSD(T)-F12 levels are practically the same. Most of the times, total energies differ further than on the fourth decimal place. Furthermore, the CCSD(T)-F12/QZ and the MkCCSD(T)-F12/QZ calculations provided identical results, the difference between them being at the 8<sup>th</sup> decimal place.

Table 3.13: Conventional and explicitly correlated total CCSD/BWCCSD/MkCCSD and CCSD(T)/BWCCSD(T)/MkCCSD(T) energies (in Hartrees) and energy differences,  $\Delta E$  (in kcal/mol), between the single reference methods and the multi-reference BWCC and MkCC approaches at a given basis set.

Basis set	CCSD	BWCCSD	MkCCSD	$\Delta E$   $\Delta E$
cc-pVDZ	-117.5286720	-117.5287050	-117.5286789	0.02   0.00 <sup>a</sup>
cc-pVTZ	-117.6482483	-117.6482595	-117.6482526	0.01   0.00
cc-pVQZ	-117.6809634	-117.6809798	-117.6809662	0.01   0.00
cc-pv5Z	-117.6907524	–	–	
CBS limit	-117.7008691	-117.7017691	-117.7017504	0.56   0.55
Basis set	CCSD(T)	BWCCSD(T)	MkCCSD(T)	$\Delta E$   $\Delta E$
cc-pVDZ	-117.5424997	-117.5425104	-117.5424989	0.01   0.00
cc-pVTZ	-117.6701862	-117.6701920	-117.6701858	0.00   0.00
cc-pVQZ	-117.7048733	-117.7048819	-117.7048731	0.01   0.00
cc-pV5Z	-117.7153170	–	–	
CBS limit	-117.7261762	-117.7271083	-117.7270977	0.58   0.58
Basis set	CCSD-F12	BWCCSD-F12	MkCCSD-F12	$\Delta E$   $\Delta E$
cc-pVDZ	-117.6527789	-117.6528096	-117.6527869	0.02   0.00 <sup>b</sup>
cc-pVTZ	-117.6812497	-117.6812607	-117.6812551	0.01   0.00
cc-pVQZ	-117.6930454	-117.6930617	-117.6930482	0.01   0.00
Basis set	CCSD(T)-F12	BWCCSD(T)-F12	MkCCSD(T)-F12	$\Delta E$   $\Delta E$
cc-pVDZ	-117.6652903	-117.6653010	-117.6652912	0.01   0.00
cc-pVTZ	-117.7023958	-117.7024014	-117.7023965	0.00   0.00
cc-pVQZ	-117.7165735	-117.7165821	-117.7165735	0.01   0.00

<sup>a</sup>The difference was less than a hundredth of a kcal/mol. Same for the other zero values in this column.

<sup>b</sup>The difference was less than a hundredth of a kcal/mol. Same for the other zero values in this column.

## Energy Profile of the Isomerisation

We are concerned with characterisation of the relative energies between cyclopropane and the two reactive species, trimethylene and propylidene, through which the isomerisation of cyclopropane is known to proceed. Over the years, there have been numerous computational studies for this reaction, but many of the reported results are outdated. Our high-level results can become a reference point for others who choose to investigate the reaction coordinate of this reaction in the future.

Table 3.14 summarises the relative energies between cyclopropane and propylidene at different levels of theory. As we can see from Table 3.14, cyclopropane is approximately 70 kcal/mol lower in energy than propylidene.

Looking at the CCSD results, we note that the variation of the relative energies is minimal throughout the basis sets used. The DZ basis set value is only 1.76 kcal/mol lower than the TZ basis value. TZ and QZ differ by 0.2 kcal/mol and the discrepancy in between the QZ and the 5Z basis sets is lower still, at 0.1 kcal/mol. At last, the CBS limit difference is less than 0.1 kcal/mol lower in energy than the 5Z basis set value. The almost non-existent variation in the relative energies along the different basis sets used means we essentially have a converged result. It appears that for the cyclopropane-propylidene relative energy, already the CCSD level of theory provides a sufficient description of the given systems.

Moving over to the BWCCSD and the MkCCSD results, the same trend in the convergence of the relative energies with respect to the basis set size is observed. DZ and TZ basis sets results are reasonably close together. Also, difference between the TZ and the QZ basis sets values is negligible. The CBS limit values are remarkably close to the QZ results, with a difference of 0.05 kcal/mol for the BWCCSD approach and all CBS limits are within 1.5 kcal/mol with respect to each other. Overall, we can say that already the TZ basis set result for any of the approaches used is very precise.

Changing the focus of our attention to the explicitly correlated relative energies, the most important thing to note is their reversed convergence trend. For example at the BWCCSD-F12 level, the relative energies drop from 71.74 kcal/mol at the DZ basis to 70.84 kcal/mol in the QZ basis. Using explicit correlation switches the convergence trend so that the CBS limit is approached

Table 3.14: Relative energies between cyclopropane and propylidene at the single and double excitations level of theory and different basis sets in kcal/mol.

Basis set	CCSD	BWCCSD	MkCCSD
cc-pVDZ	69.71	68.67	68.98
cc-pVTZ	71.47	70.22	70.67
cc-pVQZ	71.67	70.36	70.89
cc-pv5Z	71.77	–	–
CBS limit	71.84	70.41	71.01
Basis set	CCSD-F12	BWCCSD-F12	MkCCSD-F12
cc-pVDZ	73.00	71.74	72.06
cc-pVTZ	72.29	70.97	71.42
cc-pVQZ	72.18	70.84	71.37
Basis set	CCSD(T)	BWCCSD(T)	MkCCSD(T)
cc-pVDZ	70.33	69.73	70.06
cc-pVTZ	72.54	71.81	72.27
cc-pVQZ	72.79	71.99	72.53
cc-pv5Z	72.90	–	–
CBS limit	72.98	72.08	72.68
Basis set	CCSD(T)-F12	BWCCSD(T)-F12	MkCCSD(T)-F12
cc-pVDZ	73.61	72.71	73.06
cc-pVTZ	73.35	72.50	72.97
cc-pVQZ	73.29	72.45	72.99

from the other side than at the conventional level. This convergence trend reversal might be due to the F12 method being able to correct the poorly converged DZ and partially TZ basis set Hartree-Fock results.

As we can see, the values of 72.18, 70.84, and 71.37 kcal/mol for CCSD-F12, BWCCSD-F12, and MkCCSD-F12, respectively, are indeed very close to the conventional basis set limits. This is in support of the view that our results are remarkably close to being converged.

The perturbative triples results presented in Table 3.14 will wrap up our examination of the cyclopropane-propylidene energy gap. It can be observed that the differences between the CCSD and CCSD(T) levels are minimal. In fact, by including the perturbative triples correction the relative energies decrease only by 1.34 kcal/mol on average.

When we examine the MkCCSD(T)-F12 energies calculated with the DZ, TZ, and QZ basis sets, which are 73.06, 72.97, and 72.99 kcal/mol, respectively, we see an exceptional stability in the calculated values. The single reference and the BWCC calculations results are stable with respect to the basis set used as well, but to a slightly lesser extent than the MkCC values.

Let us now have a look at the relative energies between cyclopropane and trimethylene, which are displayed in Table 3.15. At the CCSD level, the values calculated with the single reference and the multi-reference MkCC and BWCC approaches differ significantly. The single reference results are approximately 20 kcal/mol higher than the multi-reference results at a given basis. The BWCC and the MkCC results are also separated from each other, by approximately 3-4 kcal/mol. Similar differences are observed for the methods employing explicit correlation.

As mentioned earlier, single reference calculations at the CCSD level are sufficient for cyclopropane in terms of precision provided, however, they are far from optimal for trimethylene. That is why the difference between the single reference approach and the multi-reference methods cyclopropane-trimethylene relative energies is as high as 20 kcal/mol. Similarly, the BWCC and the MkCC approaches perform differently for trimethylene, but provide the same results for cyclopropane.

The convergence trend of the F12 method is only partially reversed for the

Table 3.15: Relative energies between cyclopropane and trimethylene at the single and double excitations level of theory and different basis sets in kcal/mol.

Basis set	CCSD	BWCCSD	MkCCSD
cc-pVDZ	80.35	61.76	65.10
cc-pVTZ	84.29	63.91	67.72
cc-pVQZ	85.03	64.46	68.49
cc-pv5Z	85.25	–	–
CBS limit	85.36	64.38	68.57
Basis set	CCSD-F12	BWCCSD-F12	MkCCSD-F12
cc-pVDZ	87.20	65.53	68.94
cc-pVTZ	86.04	64.77	68.61
cc-pVQZ	85.87	64.98	69.02
Basis set	CCSD(T)	BWCCSD(T)	MkCCSD(T)
cc-pVDZ	61.56	55.93	60.14
cc-pVTZ	65.61	57.04	61.94
cc-pVQZ	66.49	57.19	62.38
cc-pv5Z	66.79	–	–
CBS limit	66.95	56.81	62.21
Basis set	CCSD(T)-F12	BWCCSD(T)-F12	MkCCSD(T)-F12
cc-pVDZ	72.17	60.10	64.30
cc-pVTZ	68.70	58.06	62.94
cc-pVQZ	67.90	57.78	62.95

cyclopropane-trimethylene relative energies. It can be attributed to the F12 method recovering the HF energy at the DZ and TZ basis sets to a different extent for trimethylene and cyclopropane, whereas the energy recovered at the QZ basis set is approximately same for both trimethylene and cyclopropane.

The main distinction between the perturbative triples results and the results acquired at the CCSD excitations level is in the relative proximity of the sin-

gle reference and the multi-reference BWCC and MkCC results, which is 5.45 kcal/mol on average at the conventional level and 8.57 kcal/mol with explicit correlation included. This is due to the perturbative triples correction being able to account for much of the static correlation for trimethylene.

Looking at the MkCCSD(T)-F12 results, the stability for the cyclopropane-propylidene relative energies with respect to the basis set is not retained for the cyclopropane-trimethylene relative energies at the DZ basis set. However, the MkCCSD-F12 results seem to maintain that stability, with all DZ-QZ basis set results being very close to each other. There are two reasons why the stability of the results is better at the CCSD level. Firstly, the perturbative triples correction is only performed at the conventional level, even when being part of the F12 method. Secondly, utilising basis sets of small size, such as the DZ basis set, in calculations which include explicit correlation is known to yield unreliable results, especially when perturbative triples correction is included.

Note that the relative energy CBS limits in Table 3.15 were calculated as the difference in the total energy CBS limits of cyclopropane and trimethylene. Estimation of the CBS limit for either trimethylene or cyclopropane was probably less precise than the other CBS limit and that is why the BWCC and the MkCC CBS limits are lower in energy than the respective QZ basis set results.

Table 3.16 shows our results at different levels of theory at the basis sets of best accessible quality and the results collected from literature as well. Looking at the literature data, the TCSCF result might be discarded straight away as too inaccurate, being approximately 20-30 kcal/mol off the other results. On the other hand, the MRCISD/6-31G\* value has found its place in between our BWCCSD(T)-F12/QZ and MkCCSD(T)-F12/QZ, and the MRCISD+Q/6-31G\* result of 62.42 kcal/mol closes in on the MkCCSD(T)-F12/QZ 62.95 kcal/mol. Both the MRCISD and the MRCISD+Q at the TZ2P level provide very accurate results, which is confirmed when they are compared to our results.

On a different note, if we look at the Moller-Plesset results, the UMP2 and the UMP4, we see that UMP2 is very close to our MkCCSD/QZ result. However, the reliability of the MP2 results is questionable, because they are known for overshooting the energies. The UMP4/6-31G\*\* result of 64.91 kcal/mol, which is almost identical to our BWCCSD-F12/QZ value of 64.98 kcal/mol, is more reliable. The MRCISD(T)+Q/6-31G\*\* and the MRCCSD(T)/6-31G\*\* re-

Table 3.16: Comparison of our results with the literature results for trimethylene.

**Current Study**

Computational Level	Rel. Energy	Computational Level	Rel. Energy
CCSD/5Z	85.25	CCSD(T)/5Z	66.79
BWCCSD/QZ	64.46	BWCCSD(T)/QZ	57.19
MkCCSD/QZ	68.49	MkCCSD(T)/QZ	62.38
CCSD-F12/QZ	85.87	CCSD(T)-F12/QZ	67.90
BWCCSD-F12/QZ	64.98	BWCCSD(T)-F12/QZ	57.78
MkCCSD-F12/QZ	69.02	MkCCSD(T)-F12/QZ	62.95

**Literature Data**

Computational Level <sup>a</sup>	Rel. Energy	Computational Level <sup>b</sup>	Rel. Energy
TCSCF/TZ2P	42.43	UMP2/6-31G**	68.21
MRCISD/6-31G*	59.98	UMP4/6-31G**	64.91
MRCISD+Q/6-31G*	62.42	UMRCISD(T)+Q/6-31G**	63.70
MRCISD/DZP	57.51	UCCSD(T)/6-31G**	63.72
MRCISD+Q/DZP	60.12	UBecke3LYP	60.85
MRCISD/TZ2P	57.91	MkPT2/TZ <sup>c</sup>	72.10
MRCISD+Q/TZ2P	60.28	MkCCSD/TZ	67.70

<sup>a</sup>All results in this column were calculated by Baldwin *et. al* [83].

<sup>b</sup>First five results in this column are taken from Reference [99].

<sup>c</sup>This result and the result below is by H. Bachorz [100].

sults, which are almost identical to one another, are of even better quality. The 63.70 and the 63.72 kcal/mol values are closely matching our BWCCSD/TZ result of 63.91 kcal/mol.

The DFT Becke3LYP result is closest to our BWCCSD(T)-F12/DZ result of 60.10 kcal/mol. Nonetheless, claiming that DFT with this specific functional could provide results of BWCCSD(T)-F12 quality in general would be far fetched.

The Mukherjee perturbative theory up to second order result at the TZ level of 72.10 kcal/mol is very close to our CCSD(T)-F12/DZ value of 72.16 kcal/mol. Again, in this case more data would be required to judge how reliable results can the MkPT2 theory provide overall for this system.

Finally, the MkCCSD/TZ result of 67.70 kcal/mol is virtually identical to our MkCCSD/TZ result of 67.72 kcal/mol, which is to be expected at the same level of theory and the same quality of the basis set.

Moving on to the comparison of the energy difference between cyclopropane and propylidene calculated by us with the scarce literature results, Table [3.17](#) summarises the data.

The CCSD/DZP value of 70.9 kcal/mol is actually more than 1 kcal/mol higher than our CCSD/DZ result, still surpassing our CCSD(T)/DZ value of 70.33 kcal/mol, but being lower approximately by 0.5 kcal than our CCSD/TZ result. Looking at the CCSD/TZ2P result of 69.8 kcal/mol, as well as the CCSD(T)/TZ2P result of 69.2 kcal/mol, it seems that the convergence trend is the opposite than in our single reference calculations, with the energy decreasing as basis sets of increasing quality are used and higher levels of theory are applied. The opposite convergence trend also results in the relative energies being rather comparable in magnitude to our BWCCSD calculations, with the energies located in between our BWCCSD/DZ and BWCCSD/TZ results.

Table 3.17: Comparison of our results with the literature results for propylene.

**Current Study**

Computational Level	Rel. Energy	Computational Level	Rel. Energy
CCSD/5Z	71.77	CCSD(T)/5Z	72.90
BWCCSD/QZ	70.36	BWCCSD(T)/QZ	71.99
MkCCSD/QZ	70.89	MkCCSD(T)/QZ	72.53
CCSD-F12/QZ	72.18	CCSD(T)-F12/QZ	73.29
BWCCSD-F12/QZ	70.84	BWCCSD(T)-F12/QZ	72.45
MkCCSD-F12/QZ	71.37	MkCCSD(T)-F12/QZ	72.99

**Literature Data**

Computational Level <sup>a</sup>	Rel. Energy	Computational Level	Rel. Energy
CCSD/DZP	70.9	CCSD(T)/TZ2P	69.2
CCSD/TZ2P	69.8		

<sup>a</sup>Results by Bettinger *et. al* [59].

## Conclusions

Performance of the explicitly correlated versions of the Mukherjee's multi-reference coupled cluster approach and Brillouin-Wigner multi-reference coupled cluster method was tested on the isomerisation of cyclopropane to propene through a trimethylene/propylidene diradical. Main aim of the calculations was to assess the convergence trend of MkCC-F12 and BWCC-F12 total and relative energies with respect to the quality of the basis sets used.

Compared to the conventional MkCC and BWCC approaches, the MkCC-F12 and BWCC-F12 methods provide a significant improvement in the basis set convergence of energy. The cc-pVnZ total energies were of the quality of cc-pV(n + 1)Z conventional energies. However, the theoretical prediction that employing explicit correlation should yield three orders of magnitude improvement was not reached. In order to further enhance the convergence improvement provided by the F12 method, the use of specifically designed cc-pVnZ-F12 basis sets and utilisation of the CABS approach are needed. In our case, the cc-pVnZ-F12 basis sets were not employed because of some known problems with their diffuse functions which are yet to be solved. The CABS approach could not be used in this work because it is not implemented in the MkCC-F12/BWCC-F12 methods yet.

In terms of relative energies, the convergence improvement of the MkCC-F12 and BWCC-F12 energies was not as significant as for the total energies, mainly due to the fortuitous error cancelation at the conventional level of cal-

culations.

Performance of the MkCC-F12 and BWCC-F12 methods was generally slightly better (especially in the smaller basis sets) at the CCSD level than at the CCSD(T) level, i.e. with the perturbative triples included. Incorporation of the CABS approach into the MkCC-F12 and BWCC-F12 methods should secure more reliable results, especially at the CCSD(T)/DZ level.

# Appendix A - Optimised Geometry Parameters

Figure 5.1: Trimethylene

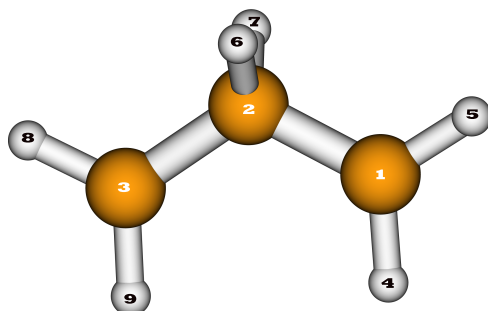


Table 5.1: Optimised geometry parameters for trimethylene.  $R_{ab}$  represents the distance between atoms  $a$  and  $b$ , and  $\alpha_{abc}$  stands for angle between atoms  $a$ ,  $b$ , and  $c$  (also for propylidene and cyclopropane).

$R_{51}$	$R_{41}$	$R_{12}$	$R_{26}^a$	$\alpha_{415}$	$\alpha_{123}$	$\alpha_{627}$
1.080	1.077	1.482	1.098	118.5	118.1	103.4

<sup>a</sup> $R_{51} = R_{93}$ ;  $R_{41} = R_{38}$ ;  $R_{12} = R_{23}$ ;  $R_{26} = R_{27}$

Figure 5.2: Propylidene

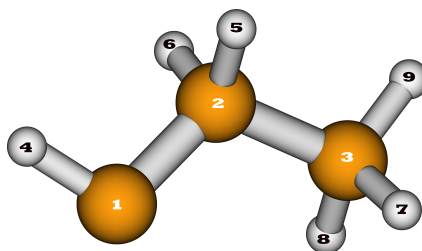


Table 5.2: Optimised geometry parameters for propylidene.

$R_{41}$	$R_{12}$	$R_{25}$	$R_{23}$	$R_{37}^a$	$\alpha_{412}$	$\alpha_{123}$	$\alpha_{526}$	$\alpha_{237}$	$\alpha_{738}$
1.103	1.478	1.098	1.528	1.087	105.5	113.6	111.2	110.4	108.4

<sup>a</sup> $R_{25} = R_{26}$ ;  $R_{37} = R_{38} = R_{39}$

Figure 5.3: Cyclopropane

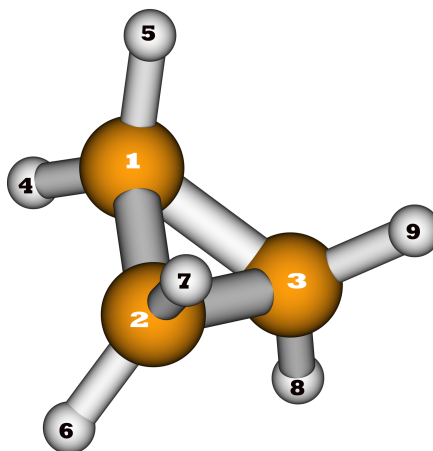


Table 5.3: Optimised geometry parameters for cyclopropane.

$R_{41}$	$R_{12}$	$\alpha_{415}$
1.078	1.502	114.8

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