Reactions of Three-Ring Molecules and Molecules with Multiple Bonds: An OVB Analysis (Orthogonal Valence Bond)

Master Thesis

Supervisor: Ao.Univ.-Prof.i.R. Dr.phil. Alexander Sax

Institute: Physical and Theoretical Chemistry

Submission Date: 16.06.2020

Author: Nina Strasser, BSc

Student Number: 01606962

E-Mail: nina.strasser@edu.uni-graz.at

1 Statutory Declaration

Ich erkläre an Eides statt, dass ich die vorliegende Arbeit selbstständig verfasst, andere als die angegebenen Quellen/Hilfsmittel nicht benutzt, und die den benutzten Quellen wörtlich und inhaltlich entnommenen Stellen als solche kenntlich gemacht habe. Das in TUGRAZonline hochgeladene Textdokument ist mit der vorliegenden Masterarbeit identisch.

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources. The text document uploaded to TUGRAZonline is identical to the present master's thesis.

Graz, 16.06.2020

(Place, date)

Nina Sh

(Signature)

2 Abstract

Elementary chemical reactions are characterized by charge and spin redistributions in relatively small spatial regions. Wave functions that are flexible enough to describe such local processes are MCSCF wave functions, however, when such wave functions are built with delocalized orbitals local effects are hidden. The use of localized orbitals reveals local changes in the molecular electron distributions. Valence bond (VB) wave functions are of this kind. Since orthogonal transformations in the space of occupied orbitals do not change the description of a quantum state, localization of delocalized orbitals by use of orthogonal transformations allows to transform an MCSCF wave function into a VB type wave functions that reveal the local spin and charge distributions. A VB wave function built with orthogonal localized orbitals is called an orthogonal valence bond (OVB) wave function.

In this thesis, a recently developed OVB method is used to investigate dissociation of a triple bond and of a double bond and the elimination of carbene and silylene from four three-ring molecules and the respective reverse reactions. By adding a carbene like molecule to a double bond, the π-bond is broken and two single bonds are created. This is only possible when both reactants are in local high spin states with unpaired electrons that are needed for bond making. The OVB analysis of the reactions shows the costs for bringing the reactants into the high spin states and it shows how change of the symmetry of the reacting system influences the overall reaction.

3 Kurzfassung

Für chemische Elementarreaktionen sind Ladungs- und Spinreorganisationen in relativ kleinen Raumbereichen charakteristisch. MCSCF Wellenfunktionen sind flexibel genug, um solche lokalen Prozesse zu beschreiben, jedoch bleiben diese verborgen, wenn die Wellenfunktion mit delokalisierten Orbitalen gebildet wird. Verwendet man jedoch lokalisierte Orbitale, werden lokale Änderungen in der Elektronenverteilung des Moleküls sichtbar gemacht. Valence Bond (VB) Wellenfunktionen leisten das. Da orthogonale Transformationen im Raum der besetzten Orbitale die Beschreibung eines Quantenzustands nicht beeinflussen, kann durch solche Transformationen eine MCSCF Wellenfunktion in eine VB-artige Wellenfunktion transformiert werden, die die lokalen Spin- und Ladungsverteilungen sichtbar macht. Eine VB Wellenfunktion, die mit orthogonalen, lokalisierten Orbitalen gebildet wird, wird eine orthogonale Valence Bond (OVB) Wellenfunktion genannt.

In dieser Arbeit wird eine kürzlich entwickelte OVB Methode zur Untersuchung der Dissoziation einer Dreifach- und einer Doppelbindung verwendet, weiters der Elimination von Carben und Silylen aus vier Dreiringmolekülen, sowie der jeweiligen Umkehrreaktionen. Bei der Addition eines carbenartigen Moleküls an eine Doppelbindung wird die π-Bindung gebrochen und zwei Einfachbindungen gebildet. Das ist nur möglich, wenn beide Reaktanten in lokalen High-Spin Zuständen mit ungepaarten Elektronen sind, die für die Bindungsbildung benötigt werden. Die OVB Analyse der Reaktionen zeigt die Kosten auf, die notwendig sind, um die Reaktanten in die High-Spin-Zustände zu bringen und sie zeigt, wie eine Änderung der Symmetrie des reagierenden Systems die Gesamtreaktion beeinflusst.

4 Acknowledgement

First of all, I would like to thank my supervisor Prof. Alexander Sax who was continuously supporting me in every step during the writing of this master thesis. I am very grateful for his accurate comments which were of critical importance. I especially want to thank him for promoting my interest in computational and theoretical chemistry.

I dedicate this work to my beloved parents Elisabeth and Manfred who are always there for me. I want to thank you so much for your moral and financial support during my studies.

Contents

1 **Statutory Declaration** **1**

2 **Abstract** **2**

3 **Kurzfassung** **3**

4 **Acknowledgement** **4**

5 **Introduction** **13**

6 **Conceptual Procedure of an OVB Analysis** **15**

7 **Comparision of the VB, MO and OVB Method** **20**

7.1 VB Wave Functions 21

7.2 MO Wave Functions 24

7.3 CI Wave Functions and Description of Reactions 27

8 **The Localization Method** **29**

9 **Results and Discussion** **30**

9.1 OVB Analysis of Multiply-Bonded Systems 32

9.1.1 Recombination Reaction of two Imidogen Fragments to Diazene in C_{2h} Symmetry 33

9.1.2 Recombination Reaction of two Nitrogen Atoms in D_{2h} Symmetry 36

9.2 OVB Analysis of Three-Ring Systems 38

9.2.1 Addition Reaction of Ethylene and Carbene to Cyclopropane in C_{2v} and C_s Symmetry 42

9.2.2 Addition Reaction of Disilene and Silylene to Cyclotrisilane in C_{2v} and C_s Symmetry 50
9.2.3 Addition Reaction of Ethylene and Silylene to Silacyclopropane in C_{2v} and C_s Symmetry 57
9.2.4 Addition Reaction of Disilene and Carbene to Disilacyclopropane in C_{2v} and C_s Symmetry 64
9.2.5 Addition Reaction of Silaethene and Carbene to Silacyclopropane in C_s Symmetry 71
9.2.6 Addition Reaction of Silaethene and Silylene to Disilacyclopropane in C_s Symmetry 75

10 Computational Details **79**

11 Conclusion **80**

A Appendix **87**
A.1 Shorthand Notation for the Slater Determinant 87
A.2 Performing Symmetry Operations on Molecules, AOs and MOs 88
A.3 Woodward-Hoffmann Rules 91

List of Figures

1 Overview of all necessary steps for carrying out an OVB calculation . . . 18

2 Three possible types of PECs . . . 31

3 PEC for the dimerization reaction to diazene . . . 33

4 Bond distances and angles for the dimerization reaction to diazene . . . 34

5 Results of the OVB analysis for the dimerization of two imidogen fragments to diazene . . . 35

6 PEC for the recombination of two nitrogen atoms . . . 36

7 Results of the OVB analysis for the recombination of two nitrogen atoms . . . 37

8 Definition of the bond angles, the out-of-plane angles and the reaction coordinate for the three-ring molecules . . . 40

9 PECs for the addition reaction of ethylene and carbene to cyclopropane in C_{2v} symmetry . . . 42

10 Bond angles and bond lengths of carbene and ethylene for the addition reaction to cyclopropane in C_{2v} symmetry . . . 43

11 Results of the OVB analysis for the addition reaction of ethylene and carbene to cyclopropane in C_{2v} symmetry . . . 44

12 PECs for the addition reaction of ethylene and carbene to cyclopropane in C_s symmetry . . . 45

13 Bond angles and bond lengths for carbene and ethylene for the addition reaction to cyclopropane in C_s symmetry . . . 46

14 Distance between the carbon atoms of carbene and ethylene and the deviation of carbene from planarity for the addition reaction to cyclopropane in C_s symmetry . . . 47

15 Results of the OVB analysis for the addition reaction of ethylene and carbene to cyclopropane in C_s symmetry 48
16 PECs for the addition reaction of disilene and silylene to cyclotrisilane in C_{2v} symmetry 50
17 Bond angles and bond lengths for silylene and disilene for the addition reaction to cyclotrisilane in C_{2v} symmetry 51
18 Results of the OVB analysis for the addition reaction of disilene and silylene to cyclotrisilane in C_{2v} symmetry 52
19 PECs for the addition reaction of disilene and silylene to cyclotrisilane in C_s symmetry 53
20 Bond angles and bond lengths for silylene and disilene for the addition reaction to cyclotrisilane in C_s symmetry 54
21 Distance between the silicon atoms of silylene and disilene and the deviation of silylene from planarity for the addition reaction to cyclotrisilane in C_s symmetry 55
22 Results of the OVB analysis for the addition reaction of disilene and silylene to cyclotrisilane in C_s symmetry 56
23 PEC for the addition reaction of ethylene and silylene to silacyclopropane in C_{2v} symmetry 57
24 Bond angles and bond lengths of silylene and ethylene for the addition reaction to silacyclopropane in C_{2v} symmetry 58
25 Results of the OVB analysis for the addition reaction of ethylene and silylene to silacyclopropane in C_{2v} symmetry 59
26 PEC for the addition reaction of ethylene and silylene to silacyclopropane in C_s symmetry 60
27 Bond angles and bond lengths of silylene and ethylene for the addition reaction to silacyclopropane in C_s symmetry 61

28 Distance between the silicon atom of silylene and the carbon atoms of ethylene and the deviation of silylene from planarity for the addition reaction to silacyclopropane in C_s symmetry . 62
29 Results of the OVB analysis for the addition reaction of ethylene and silylene to silacyclopropane in C_s symmetry 63
30 PEC for the addition reaction of disilene and carbene to disilacyclopropane in C_{2v} symmetry 64
31 Bond angles and bond lengths of carbene and disilene for the addition reaction to disilacyclopropane in C_{2v} symmetry . . . 65
32 Results of the OVB analysis for the addition reaction of disilene and carbene to disilacyclopropane in C_{2v} symmetry 66
33 PECs for the addition reaction of disilene and carbene to disilacyclopropane in C_s symmetry 67
34 Bond angles and bond lengths of carbene and disilene for the addition reaction to disilacyclopropane in C_s symmetry 68
35 Distance between the carbon atom of carbene and the silicon atoms in disilene and the deviation of carbene from planarity for the addition reaction to disilacyclopropane in C_s symmetry 69
36 Results of the OVB analysis for the addition reaction of disilene and carbene to disilacyclopropane in C_s symmetry 70
37 PEC for the addition reaction of silaethene and carbene to silacyclopropane in C_s symmetry 71
38 Bond angles and bond lengths of carbene and silaethene for the addition reaction to silacyclopropane in C_s symmetry . . . 72

39 Distance between the carbon atom of carbene and the heavy atoms of silaethene and the deviation of carbene from planarity for the addition reaction to silacyclopropane in C_s symmetry 73

40 Results of the OVB analysis for the addition reaction of silaethene and carbene to silacyclopropane in C_s symmetry 74

41 PEC for the addition reaction of silaethene and silylene to disilacyclopropane in C_s symmetry 75

42 Bond angles and bond lengths of silylene and silaethene for the addition reaction to disilacyclopropane in C_s symmetry . . 76

43 Distance between the silicon atom of silylene and the heavy atoms of silaethene and the deviation of silylene from planarity for the addition reaction to disilacyclopropane in C_s symmetry 77

44 Results of the OVB analysis for the addition reaction of silaethene and silylene to disilacyclopropane in C_s symmetry 78

45 Definition of the positions of two symmetry equivalent atoms . 88

46 Adding of the respective s AOs on the atoms A and B 89

47 Adding of the p_z and p_x AOs on the atoms A and B 90

48 Formation of the delocalized MOs that describe a double bond via LCAO 91

49 The symmetry elements for the dimerization of XH_2 in D_{2h} symmetry 93

List of Tables

1 Comparision of the numbers of configuration with different spin multiplicities . . . 16

2 Comparision of the numbers of configuration with different spin multiplicities . . . 26

3 Comparision of the bond lenght of the imidogen fragment . . . 34

4 Comparision of the geometry parameters of carbene and silylene 39

5 Overview of the reaction energies and the energies of the barriers 41

6 Summary of the transformation behaviour of the localized AOs 89

7 Summary of the transformation behaviour of the delocalized MOs . . . 91

8 Mapping of the four reactant AOs used in the dimerization of XH_2 fragments . . . 93

9 Symmetry labels of the orbitals involved in the XH_2 dimerization reaction . . . 94

List of Abbreviations

AO	Atomic Orbital
CAS	Complete Active Space
CASSCF	Complete Active Space Self-Consistent Field
CI	Configuration Interaction
CSF	Configuration State Function
FCI	Full Configuration Interaction
FO	Fragment Orbital
FORS	Fully Optimized Reaction Space
HF	Hartree-Fock
HL	Heitler-London
HOMO	Highest Occupied Molecular Orbital
IRREP	Irreducible Representation
LC	Linear Combination
LCAO	Linear Combination of Atomic Orbitals
LFO	Localized Fragment Orbital
LP	Lone Pair
LUMO	Lowest Unoccupied Molecular Orbital
MCSCF	Multi-Configurational Self-Consistent Field
MO	Molecular Orbital
OVB	Orthogonal Valence Bond
PEC	Potential Energy Curve
VB	Valence Bond

5 Introduction

The topic of this work is the description of chemical reactions. Levine[1] is firmly convinced that reactivity is a local effect, because in elementary reactions the valence electrons of mostly two, seldom three or more atoms are involved. The HF method is unable to correctly describe the breaking or making of new bonds, because these processes involve spin and charge reorganization, which cannot be represented by wave functions in which orbitals are always doubly occupied. Any reorganization of the electronic structure involves a correlation of the motion of the electrons, which can only be described by so-called correlation methods that use multi-configurational wave functions. MCSCF is the method of choice for the description of chemical reactions, especially in the CASSCF version[2, 3], also known as FORS.[4, 5, 6, 7, 8, 9, 10] If the active orbital space and the number of active electrons are correctly chosen, such wave functions are able to describe the electron redistribution during a chemical reaction. However, by the use of delocalized MOs all local processes in such reactions are hidden and must be extracted from the wave functions. The OVB method provides a way to reveal these local properties. For simplicity reasons, only closed-shell systems are considered in this thesis.

The main focus of this study lies on the investigation of dissociation and elimination reactions and the respective reverse recombination and insertion reactions. As examples for reactions involving two reactive centers, the dissociation of double bonds in diazene and of the triple bond in dinitrogen are studied. Three reactive atoms occur when a carbene-like fragment is eliminated from three-ring molecules, the molecules cyclopropane, cyclotrisilane, silacyclopropane and disilacyclopropane were studied. On the basis of these molecular systems the different reactivities of the elements nitrogen, carbon and silicon are discussed. The study of the three-center problems allows also to ask the following questions: Do these molecules react in high or in low symmetry? Are these reactions one-step or two step reactions, or, in other words, are the reactions concerted or non-concerted? OVB analysis of the wave functions allows to answer these questions.

6 Conceptual Procedure of an OVB Analysis

The theoretical basis of the so called OVB analysis of a CASSCF wave function is given in recent papers by Sax[11, 12] and applied to chemical reactions in Ref.[13]. The essential prerequisite for an OVB analysis of a CASSCF wave function is the partitioning of a molecular system, in short, the molecule, into subsystems, called the fragments. In chemical reactions, fragments may be educts or products. By this partitioning, one defines which bonds in the molecule are broken or created. The electrons involved in these bonds are the active electrons, the bonding and antibonding orbitals describing these bonds are the active orbitals. This is the step where reaction mechanisms of different complexity can be designed.

To describe the breaking of a bond between two atoms, the wave function describing the system must allow the character of occupied orbitals to change smoothly from bonding to antibonding, otherwise no dissociation can be correctly described. HF wave functions do not have this property, because in closed-shell RHF, occupied orbitals in a Slater determinant are always doubly occupied, whereas virtual orbitals are never occupied; in open-shell RHF some orbitals may also be singly occupied. If such a wave function is used to describe a chemical reaction, there is either never a change in the occupancy of the occupied orbitals, or a change occurs abruptly in a so-called orbital flip but not in a continuous way. HF wave functions are therefore unable to describe chemical reactions, where bonds are broken or newly formed. However, properly designed CI wave functions are able to do this.

A CI wave functions is a multi-configurational wave function, which is a LC of Slater determinants. Since Slater determinants are, in general, not eigenfunctions of the total spin operator, but only eigenfunction of the spin projection, a CI wave function is, in general, neither an eigenfunction of the total spin operator nor of the spin projection operator.[14] It is however possible to construct eigenfunctions of the total spin operator CSFs as LCs of Slater determinants, then a CI wave function that is a LC of CSFs is also an eigenstate of the total spin operator. The number $n(N, m, S)$ of possible CSFs that can be constructed depends for N active electrons, m active orbitals and a spin state with quantum number S is given by the Weyl formula, Equation 1.[15]

$$n(N, m, S) = \frac{2S+1}{m+1} \binom{m+1}{\frac{1}{2}N - S} \binom{m+1}{\frac{1}{2}N + S + 1} \tag{1}$$

Table 1 shows the number of determinants that can be made with equal number of electrons and orbitals ($N = m$) and the number of corresponding singlet CSFs ($S = 0$).

Table 1: Comparision of the numbers of configuration that can be generated from determinants with different spin multiplicities.

$N = m$	**Number of determinants that can be made with N active electrons in m active orbitals**	**Number of singlet states for N active electrons in m active orbitals**
2	6	3
4	70	20
6	924	175
8	12870	1764
10	184756	19404

If the CI wave function is a LC of all possible CSFs, one speaks of a FCI wave function over the active orbital space. Only FCI wave function have the property that the described state is invariant under orthogonal transformations in the active orbital space.

Conventional CI wave functions are made with orbitals that are optimized using a single Slater determinant. In contrast, an MCSCF wave function is a CI wave function made with orbitals that are optimized for this CI wave function. If the CI wave function is a FCI wave function for a spin state with quantum number S made with $n(N, m, S)$ CSFs, one speaks of a CAS(N, m) wave function, that means CAS by distributing N electrons among m orbitals. If, for whatever reasons, only a subset of all possible CSFs is used, one speaks of a selected MCSCF wave function. Because such wave functions are not invariant under orthogonal transformations, selected wave functions are notorious for jumps in the total energy.[16]

The active space, necessary to correctly describe the breaking of N bonds, consists of $2N$ active orbitals, a bonding and a corresponding antibonding orbital for each bond and $2N$ active electrons distributed among them. To describe the dissociation of a single bond, a CAS(2,2) wave function is necessary, which is a LC of three CSFs. For the dissociation of a double bond one needs a CAS(4,4) wave function made of 20 CSFs and so on. These wave function are considered to be of the lowest level necessary to give a correct description of the dissociation process. This is the reason, why CAS wave functions are also called FORS wave functions.

If, by an orthogonal transformation, the delocalized molecular orbitals are localized on the predefined fragments, bonding and antibonding molecular orbitals are transformed into atom centered LP FOs.

All calculations that result in an OVB calculation comprise a total of five

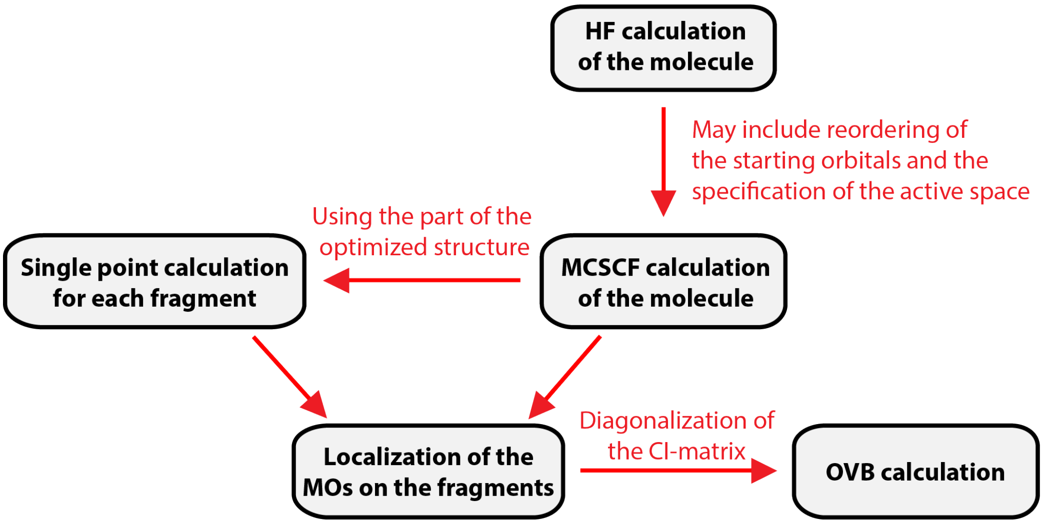

Figure 1: Overview of all necessary steps for carrying out an OVB calculation.

steps, which are shown schematically in Figure 1. In the first step, the sets of active and doubly occupied orbitals are selected from the orbitals obtained from a HF calculation, and used as starting orbitals for the following CASSCF calculation, which is step two. With this CASSCF wave function, the geometry of the molecule is optimized.

In the third step, for each fragment at the atomic positions in the CASSCF optimized molecular geometry, FOs are calculated with low-level methods and the same basis set as used for the CASSCF calculation.

In the fourth step, the delocalized CASSCF orbitals are localized on the fragments using an orthogonal transformation, by which the CASSCF orbitals are made as similar as possible to the FO calculated in step three.

In the fifth step, the LFOs are used to set up a FCI wave function with the same CSFs as used in the CASSCF wave function. Since the transformation from delocalized MOs to LFOs is an orthogonal transformation, both FCI wave functions describe the same molecular state, meaning that both state energies are equal. The CI coefficients of the investigated molecular state, mostly the ground state, represent the weights of the CSFs in the state. The diagonal elements of the Hamiltonian, which are the energy expectation values of the CSFs, allow a ranking of the energetic importance of the CSFs. CI coefficients and CSF energies are the information that are needed for an OVB analysis of an CASSCF wave function.[11]

Because delocalized active MCSCF orbitals are transformed into LP FOs, the transformed CSFs resemble VB CSFs, which, by construction, represent local charge and spin distributions. In contrast to conventional VB wave functions, which are made with non-orthogonal atom centered AOs or hybrid AOs, the orbital transformation yields wave functions made with orthogonal FOs and therefore one speaks of orthogonal VB or OVB. OVB wave function reveal local effects of chemical reactions that are hidden when wave functions with delocalized orbitals are used.

7 Comparision of the VB, MO and OVB Method

Wave function methods come in two different flavors, VB and MO methods. See, McWeeny[14], chapters 3 and 7. In VB methods the smallest building blocks are orbitals that are one-electron functions and mostly localized on atoms, for example AOs, or, less frequent, on fragments of a molecule, so-called FOs. MO methods, on the other hand, are always based on orbitals delocalized over the whole molecule. MOs that are eigenvectors of a Hermitian operator, e.g., the Fock operator from HF theory, or effective Hamiltonians, are always orthogonal to each other, whereas AOs are always non orthogonal. FOs are in general delocalized over the fragments, but FOs from different fragments need not to be orthogonal to each other. Both methods describe many-electron systems by Slater determinants, that is antisymmetrized products of orbitals, but the way of constructing the wave functions is very different.

MO theory describes the electron structure of molecules in the same way as it is done for many-electron atoms: One assumes that there are one-electron states that can be distinguished by their state energies (orbital energies) and that the electronic ground state is obtained by filling up the energy-ordered orbitals with maximally two electrons (Aufbau principle) having different spin projection, that is one alpha and one beta electron. For systems with a non-degenerate ground state, a single Slater determinant is sufficient to describe the ground state in zeroth order. For a system with $2N$ electrons the wave function represented by a single Slater determinant made with the orbitals ψ. The construction of this wave function is given by Equation 2.[14]

$$\Psi(1, \cdots, 2N) = |\psi_1(1)\overline{\psi_1(2)}\psi_2(3)\overline{\psi_2(4)}\cdots\psi_N(2N-1)\overline{\psi_N(2N)}| \quad (2)$$

This is a so-called closed-shell wave function. It is an eigenfunction of the $\hat{S}_z$ and of the $\hat{S}^2$ operators for spin quantum numbers $s = 0$ and $m_s = 0$, that is a single state. If some of the MOs are only singly occupied but the number of alpha and beta electrons is equal or if not all components of degenerate orbitals are doubly occupied, a single Slater determinant is an eigenfunction of the $\hat{S}_z$ operator but not of the $\hat{S}^2$ operator. By making proper LC of such Slater determinants one gets eigenfunctions of the $\hat{S}^2$ operator. The excited singlet state resulting from an excitation of one electron from orbital ψ_N into orbital ψ_{N+1} is represented in lowest order by the following LC:

$$\frac{1}{\sqrt{2}}(|\psi_1(1)\overline{\psi_1(2)}\psi_2(3)\overline{\psi_2(4)}\cdots\psi_N(2N-1)\overline{\psi_{N+1}(2N)}|-$$

$$|\psi_1(1)\overline{\psi_1(2)}\psi_2(3)\overline{\psi_2(4)}\cdots\overline{\psi_N}(2N-1)\psi_{N+1}(2N)|)$$

7.1 VB Wave Functions

VB wave functions represent the chemist's view that covalent bonding in molecules is the result of the formation of singlet coupled electron pairs.[18] According to this view, two atoms are connected by a (single) bond, if each atom contributes a single electron to the pair, one atom contributes an alpha electron, located in AO a and atom B contributes a beta electron, located in AO b. The Slater determinant describing this electron distribution is $|a(1)\bar{b}(2)| = a(1)\alpha(1)b(2)\beta(2) - b(1)\beta(1)a(2)\alpha(2)$. This Slater determinant is not an eigenfunction of the $\hat{S}^2$ operator. Due to the indistinguishability of electrons at the microscopic level this distribution has the same energy as that described by Slater determinant $|b(1)\bar{a}(2)| = -|\bar{a}(1)b(2)|$, so both determinants are degenerate and only the LC $|a(1)\bar{b}(2)| - |\bar{a}(1)b(2)|$ describes this quantum state correctly. Both Slater determinats are eigenfunctions of the $\hat{S}_z$ operator but neither of them is an eigenfunction of the $\hat{S}^2$. Considering the overlap of the two AOs, one gets the so-called HL wave function represented by Equation 3.

$$\Psi^{\mathrm{HL}} = \frac{1}{\sqrt{2(1+S^2)}}(a(1)b(2) + b(1)a(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \tag{3}$$

This HL wave function is an eigenfunction of the $\hat{S}^2$ operator. Since it is an eigenfunction to the spin quantum number $S = 0$, it is a singlet CSF.[18] Because of its form this two-electron wave function is called a geminal, exactly a singlet geminal. See Pilar[19], chapter 17. This is the well known HL wave function. The other LC of the two Slater determinants is a triplet CSF (Equation 4), which is also a geminal.

$$\Psi^{\mathrm{triplet}} = \frac{1}{\sqrt{2(1-S^2)}}(a(1)b(2) + b(1)a(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \tag{4}$$

Wave functions where both electrons reside in one AO, like $|a\bar{a}|$ and $|b\bar{b}|$, describe ionic charge distributions in anion/cation pairs. Because $|a\bar{a}|$ and $|b\bar{b}|$ are again energetically degenerate, two LCs can be made, which are both singlet CSFs (Equation 5 and 6).

$$\Psi_1^{\mathrm{ion}} = \frac{1}{\sqrt{2(1+S^2)}}(|a\bar{a}| + |b\bar{b}|) \tag{5}$$

$$\Psi_2^{\mathrm{ion}} = \frac{1}{\sqrt{2(1-S^2)}}(|a\bar{a}| + |b\bar{b}|) \tag{6}$$

One of them (Ψ_1^{ion}) has the same spatial symmetry as the HL CSF. For infinite distance between the two atoms, the overlap goes to zero and Ψ^{HL} describes two neutral atoms far apart, therefore it is called a neutral wave function. In the case of a homonuclear atom pair with equal AOs a and b, for example, the hydrogen molecule, all VB wave functions represent symmetric charge distributions.

A conceptual advantage of the HL wave functions is that they can be easily interpreted. Both the HF and the triplet geminals describe for infinite distance R between the two atoms, that is, the dissociated system, two neutral hydrogen atoms, the two wave functions are energetically degenerate, both are called neutral wave functions. Similarly, both ionic wave functions describe the same infinitely separated hydrid/proton pair, they are also degenerate. At large distances, Ψ^{HL} and Ψ_1^{ion} describe physically incompatible electronic situations (neutral vs. ionic) and are therefore orthogonal to each other. When the distance decreases, the constructive interference of the two AOs increases and the overlap integral S goes to one. For $R = 0$, the AOs are identical and the HL and the ionic wave function become identical as well.

$$\lim_{R \to 0} a = b \tag{7}$$

$$a(1)b(2) + b(1)a(2) = a(1)a(2) + a(1)a(2) = 2a(1)a(2) \tag{8}$$

$$\lim_{R \to 0} \Psi^{HL} = \lim_{R \to 0} \Psi^{ion} \tag{9}$$

At $R = 0$ Ψ^{HL} and Ψ_1^{ion} describe a united atom, that is a helium atom, with two electrons residing in a hydrogen AO in a hydrogen AO. The triplet CSF and the second ionic CSF describe two different excited states of the united atom. Because of its geminal structure the HL CSF is often called a covalent wave function, meaning each atom contributes one electron to the bonding interaction and often covalent is equated with neutral. However, due to the interference of the AOs at shorter distances, there is a shift of the electron density from each atom towards the other and the polarized atoms do no longer represent neutral atoms with spherical electron density. This density shift is essential for the bonding, and it is erroneously called charge-transfer, although no charge separation takes place.

In conventional or HL-Pauling VB methods only HL type geminals were used to describe bonding. With such a wave function the ground state of the hydrogen molecule dissociates correctly in two hydrogen atoms, the PEC has a local minimum, but both the equilibrium distance and the stabilization energy are not satisfactory. Since HF and ion have the same spatial symmetry they can be linearly combined and with such a VB CI wave function, the description of the ground state is considerably improved. Equation 10 adds this ionic part in order to improve the VB wave function. See Shaik[18], chapter 3 or Pilar[19], chapter 16.

$$\Psi^{VB} = c_{HL}\ \Psi^{\mathrm{HL}} + c_{ion}\ \Psi^{\mathrm{ion}} \tag{10}$$

7.2 MO Wave Functions

Most MO wave functions are built with HF MOs. The most simple wave function describing the hydrogen molecule consists of the doubly occupied σ orbital, $|\sigma\bar{\sigma}|$. It is a MO CSF describing a singlet spin state. Nearly all MOs cannot be represented by analytic functions but must be approximated. Most important is the LCAO approximation, which is a linear combination of basis functions located at the atoms that constitute the molecule. The most simple form of the σ MO for the hydrogen atom is given by Equation 11.

$$\sigma = \frac{1}{\sqrt{2(1+S)}}(a+b) \tag{11}$$

The Slater determinant describing the non-degenerate ground state of a molecule with an even number of electrons, say $2N$, consists of N doubly occupied MOs, $|\psi_1(1)\bar{\psi}_2(2)\cdots\psi_N(2N-1)\bar{\psi}_N(2N)|$. HF MOs are ordered according to their orbital energy, the Aufbau principle says that the filling of the orbitals with electrons starts from the orbital with the lowest orbital energy. Excited states are represented by CSFs that are built with Slater determinants where some orbitals are singly occupied, for example,

$$|\psi_1(1)\bar{\psi}_2(2)\cdots\psi_{N-1}(2N-3)\bar{\psi}_{N-1}(2N-2)\psi_N(2N-1)\bar{\psi}_{N+1}(2N)| -$$

$$|\psi_1(1)\bar{\psi}_2(2)\cdots\psi_{N-1}(2N-3)\bar{\psi}_{N-1}(2N-2)\bar{\psi}_N(2N-1)\psi_{N+1}(2N)|$$

describes an excited singlet with one electron excited from the HOMO ψ_N to the LUMO ψ_{N+1}. The Slater determinant $|\psi_1(1)\bar{\psi}_2(2)\cdots\psi_N(2N-1)\psi_{N+1}(2N)|$ is one component of the HOMO-LUMO excited triplet. To describe excited states, orbitals that are unoccupied in the ground state Slater determinant must be singly or doubly occupied, on the other hand are formerly doubly occupied orbitals only singly occupied or even empty. The orbitals that can be doubly occupied, singly occupied or empty, are called active orbitals, the number of electrons that can be placed in the active orbitals are the active electrons.

For example, if $|\sigma, \bar{\sigma}|$ is the ground state determinant, and electrons can be excited into the σ^* orbitals, that is, there are two active orbitals and two active electrons. One can make the following six Slater determinants:

$$|\sigma, \bar{\sigma}|, |\sigma, \bar{\sigma^*}|, |\sigma^*, \bar{\sigma}|, |\sigma^*, \bar{\sigma^*}|, |\sigma, \sigma^*|, |\bar{\sigma}, \bar{\sigma^*}|$$

Four of these six Slater determinants are also eigenfunctions of the $\hat{S}^2$ operator, the other two determinants must be linearly combined to get CSFs. Finally, one gets three singlet states and one triplet state, each state to the spin quantum number S has $2S+1$ components, represented by a CSF. The number of CSF n that can be generated for N active electrons, m active orbitals and the spin multiplicity S is given by the Weyl formula. Table 2 shows the number of determinants that can be made with equal number of electrons and orbitals and the number of corresponding singlet CSFs.

Table 2: Comparision of the numbers of configuration that can be generated from determinants with different spin multiplicities.

Number of electrons	**Number of determinants that can be made with N active electrons in m active orbitals**	**Number of singlet states for N active electrons in m active orbitals**
2	6	3
4	70	20
6	924	175
8	12870	1764
10	184756	19404

A wave function made by a LC of all possible CSFs is called a FCI wave function, the dimension of a FCI problem depends on the number of active orbitals, active electrons and the spin state. The method where the orbitals are optimized with a multi determinantal wave function is called the MCSCF method. If the maximum number of CSFs $n(N, m, S)$ are used, one speaks of a $CAS(N, m)$, that means CAS by distributing N electrons among m orbitals. To describe the dissociation of a single bond, a $CAS(2, 2)$ wave function is necessary, for the dissociation of a double bond one needs a $CAS(4, 4)$ wave function and so on. These wave function are considered to be of the lowest level necessary to give a correct description of the dissociation process.

7.3 CI Wave Functions and Description of Reactions

With the ground state wave function $|\sigma\bar{\sigma}|$ for the hydrogen molecule one gets an acceptable equilibrium distance and a reasonable stabilization energy relative to twice the energy of a hydrogen atom. However, when the dissociation is studied, the dissociation limit is completely wrong, the energy for $R \to \infty$ is much too high. The reason is easily found, when the Slater determinant is developed into VB CSFs (Equation 12).

$$|\sigma\bar{\sigma}| \propto (\Psi^{\mathrm{ion}} + \Psi^{\mathrm{HL}}) \tag{12}$$

The MO Slater determinant is the sum of the HL and the ion VB CSF with equal weight, independent of the distance between the atoms. The MO wave function describes also at large distance a mixture of neutral and ionic electron distribution, which is unphysical. When the antibonding MO of Equation 13 is doubly occupied, the development of the MO Slater determinant, gives again a singlet MO CSF (Equation 14). See Shaik[18], chapter 3.7.

$$\sigma^* = \frac{1}{\sqrt{2(1-S)}}(a-b) \tag{13}$$

$$|\sigma^*\bar{\sigma^*}| \propto (\Psi^{\mathrm{ion}} - \Psi^{\mathrm{HL}}) \tag{14}$$

By making LCs of the two MO CSFs (an MO CI wave function), one can either reduce the covalent VB content in the CI wave function and reduce the ionic one and vice versa. This shows, that both MO CI wave functions and VB CI wave functions are equivalent and describe the same states. For the description of chemical reactions CAS wave functions are the MO method of choice, especially because MO methods have certain computational advantages VB methods do not have. On the other hand, the interpretation of MO wave functions is much more difficult than that of VB wave functions. Since

VB wave functions are made with localized orbitals, VB CSFs describe local electron and spin distributions, in MO CSFs, such local effects are hidden by the use of delocalized MOs. For the interpretation of MO wave functions a transformation into VB wave functions would be helpful. However, the transformation from orthogonal MOs to non-orthogonal AOs is difficult and since the character of VB CSFs made with non-orthogonal AOs may depend on the spatial arrangement of the atoms in the molecular system, the interpretation is not unique. If, however, delocalized MOs are transformed into orthogonal localized orbitals, one gets a so called orthogonal VB wave function. Such wave functions can be used to analyse MO based wave functions. This is what is done in an OVB analysis of MCSCF wave functions.[12, 13]

8 The Localization Method

There are two different approaches for the localization of MOs with various criteria. The first approach uses intrinsic criteria, that is, criteria based on well defined physical properties, such as the minimization of the Coulomb interaction (Foster-Boys criterion) or the maximization of the repulsive interaction (Edminston-Ruedenberg criterion) between localized charge distributions, or the maximization of partial charges on atoms (Pipek-Mezey criterion). However, this approach has not been used in this thesis.

In the second approach, used in this thesis, an external criterion is applied, namely, the parts of the molecule on which the orbitals should be localized, the fragments, are predefined by the user.

The method used to localize delocalized MOs on predefined fragments is the non-iterative orthogonal Procrustes transformation [11] which is well known in the field of matrix analysis.[20]

The localization is separately done for the doubly occupied and active MOs, localized virtual MOs are not needed.

9 Results and Discussion

The investigated systems can be divided according to three different reaction types including the respective reverse reactions:

1. The dissociation of double bonds or the recombination of two fragments giving a double bond.
2. The dissociation of triple bonds or the recombination of two fragments giving a triple bond.
3. The elimination of a carbene-like fragment from a three-ring molecule or the addition of a carbene-like fragment to a double bond giving a three-ring molecule.

The first reaction type includes the recombination of two NH_2 fragments to diazene (N_2H_2). For the second class only the recombination to the triply bonded nitrogen molecule (N_2) is discussed. And for the third class the addition reaction of CH_2 to ethylene to form cyclopropane (c-C_3H_6), the addition of SiH_2 to disilene to form cyclotrisilane (c-Si_3H_6) and the addition of CH_2 as well as SiH_2 to silaethene for the formation of both silacyclopropan (c-SiC_2H_6) and disilacyclopropane (c-Si_2CH_6) have been studied. The discussion of the results will be based on the recombination reactions. All molecules are in their respective singlet ground states.

Before the individual systems are studied in detail, some general observations concerning the reaction types should be made. A PEC links the reactant with the desired product along a self-defined reaction coordinate. The energy profile of a chemical reaction can already give precious indications of different reactivities. According to the shapes of the PECs, there are three different types of chemical reactions with different reaction mechanisms. The first PEC in Figure 2 has only one local minimum, left of the minimum the PEC decreases monotonically, right of it the curve increases monotonically and becomes constant for large reaction coordinates R. Such PECs are found for simple recombination processes of high spin fragments. The second type of PECs in Figure 2 has also a local maximum indicating a reaction barrier, which must be overcome to that the reaction becomes possible. PECs of the third type in Figure 2 are not as smooth as those of types 1 and 2. The steps in the curve indicate non-concerted reaction mechanisms with different elementary reaction steps.[21]

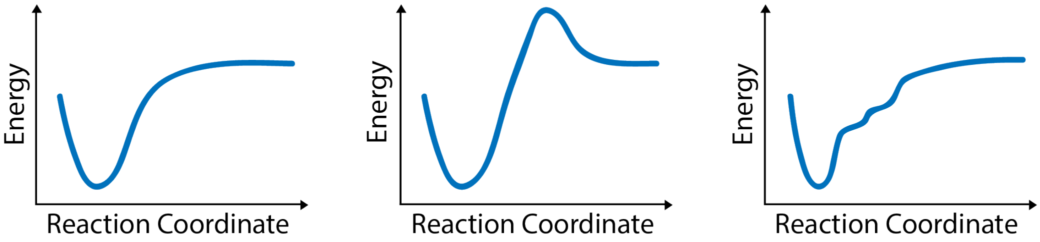

Figure 2: Three possible types of PECs that appear throughout this thesis.

9.1 OVB Analysis of Multiply-Bonded Systems

In the following chapters the dissociation and recombination reactions of dinitrogen and diazene are investigated by analyzing the PEC and using the OVB analysis for the detection of the hidden information including spin and charge reorganization during the reaction of the fragments. All molecules are composed of fragments and their geometries change during the reaction path way. Because of that, it is necessary to know the geometry parameters (e.g. bond lengths, bond angles, out-of-plane angles, etc.) of each individual fragment so that the fragments become comparable with each other.

Since geometry parameters are typical for the electronic states of molecules, monitoring of the geometry parameter of the reacting fragments helps to understand the importance of elementary processes during chemical reactions. For the recombination of the multiply-bonded systems, the important geometry parameters are the N-N and the N-H bond lengths, for diazene also the N-N-H bond angle.

9.1.1 Recombination Reaction of two Imidogen Fragments to Diazene in C_{2h} Symmetry

The next reaction is the dimerization of two imidogen fragments to trans-diazene.

$$2\ \mathrm{NH} \longrightarrow \mathrm{N_2H_2}$$

This reaction has been studied in C_{2h} symmetry using a $CAS(4,4)$ wave function. The PEC of diazene represented by Figure 3 looks very unspectacular. The reaction coordinate R is defined as the distance between the two nitrogen atoms of the imidogen fragments.

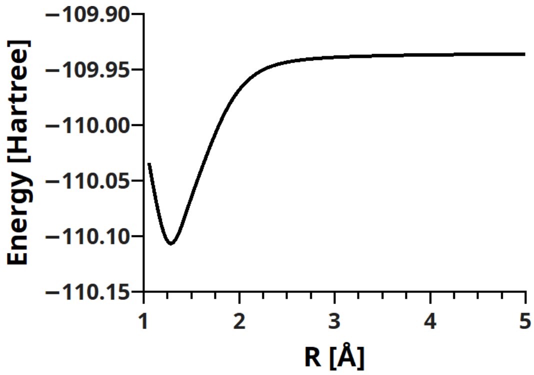

Figure 3: PEC for the dimerization reaction to diazene in C_{2h} symmetry using a CAS(4,4) wave function.

Figure 4 gives the geometry parameters. During the recombination reaction to diazene, the N-H bond lenght shrinks from 1.02 Å to 1.01 Å. Moreover, the N-N-H bond angle increases from 75 degree to 108 degree.

Table 3 summarizes the bond lenghts for the imidogen molecule in the singlet and triplet state. Both calculated bond lenghts are very similar to each

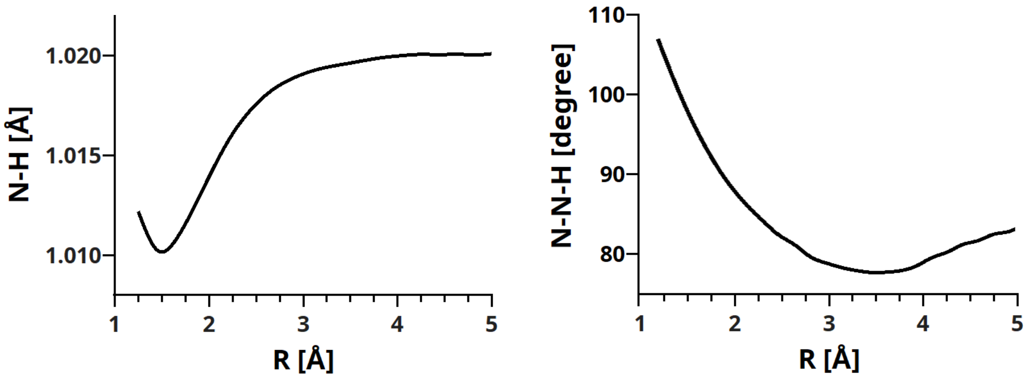

Figure 4: Bond distances (left) and angles (right) for the dimerization reaction to diazene in C_{2h} symmetry using a CAS(4,4) wave function.

Table 3: Comparision of the bond lenght of the imidogen fragment in different electronic states received with the 6-311G(d,p) basis set and the excitation from the singlet to the triplet state (ΔE_{ST}) in millihartree (mH).

	Imidogen (NH)
State Symmetry	**Bond Length (N-H) [Å]**
$^1\boldsymbol{\Sigma}$	1.019
$^3\boldsymbol{\Sigma}$	1.020
	$\boldsymbol{\Delta E_{ST}}$ **[mH]**
	-68.4

other. Calulating the lowest singlet and lowest triplet state of diazene indicates that the triplet state is the ground state. The difference of both total enegies gives a negative value for the singlet-triplet gap ΔE_{ST}.

The OVB analysis in Figure 5 reveals some interesting effects. At large distances only one particular CSF is important with a weight of nearly 100 %. It indicates that both imidogen fragments are in their respective triplet states. During the whole reaction this CSF has always the heighest weight. At a distance of 2.2 Å an ionic CSF becomes important. It represents a single charge-transfer between the s AOs of the two fragments. Furthermore, a second charge-transfer effect is induced at a distance of 1.6 Å, where one electron from the s AO moves to the p AO of the other fragment. Finally, the equilibrium geometry of diazene is decribed by a total of four CSFs. Two of them are ionic and the other ones are neutral. The non-ionic CSFs have the lowest energies, while the two ionic CSFs give higher and nearly identical energies over the whole dimerization reaction.

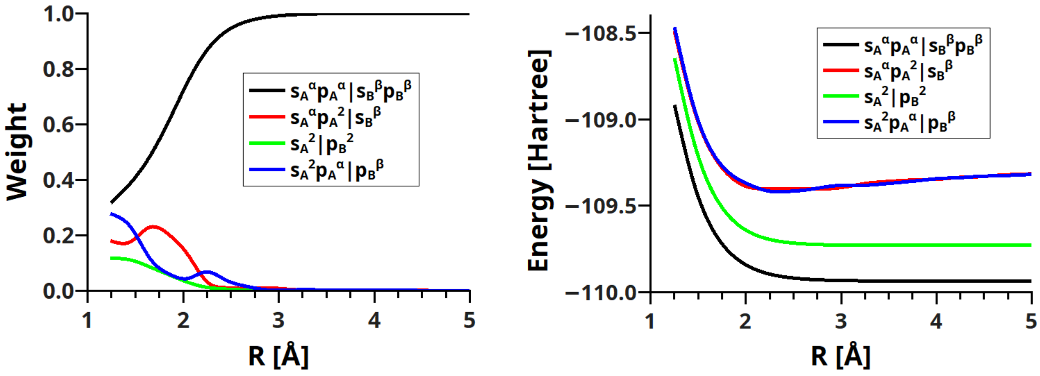

Figure 5: Results of the OVB analysis for the dimerization reaction of two imidogen fragments to diazene in C_{2h} symmetry using a CAS(4,4) wave function.

9.1.2 Recombination Reaction of two Nitrogen Atoms in D_{2h} Symmetry

The third reaction investigated is the recombination of two nitrogen atoms to the diatomic, homonuclear nitrogen molecule.

$$2\ \mathrm{N} \longrightarrow \mathrm{N}_2$$

This reaction has been performed in D_{2h} symmetry using a $CAS(6,6)$ wave function with a total of six active MOs being π_x, π_x^*, π_y, π_y^*, σ and σ^*. The computed PEC in Figure 6 looks again quite unimpressive.

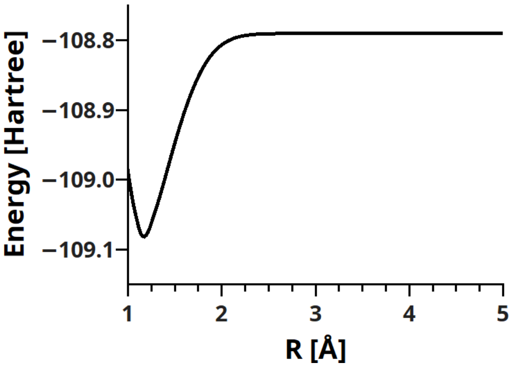

Figure 6: PEC for the recombination of two nitrogen atoms in D_{2h} symmetry using a CAS(6,6) wave function.

Figure 7 shows the results of the OVB analysis. At large distances between the two nitrogen atoms, the neutral CSF ϕ_1 that describes two high-spin fragments has a weight of 100 %. This CSF maintains the lowest energy during the whole recombination reaction. At a distance of around 2.0 Å ϕ_4 becomes important that describes a local singlet coupling in the two p orbitals. This means that there is a transition from the high-spin to the low-spin state in the nitrogen atoms. The tendencies towards the formation of the σ bond and the two additional bonds required for the triple bond remain

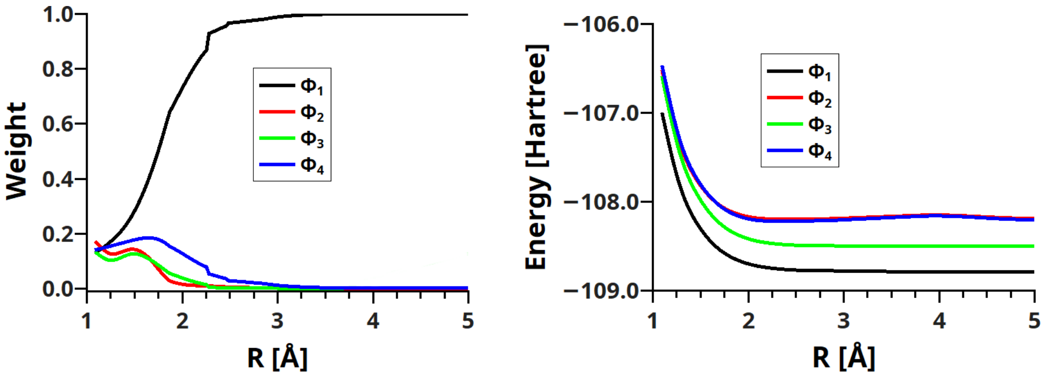

Figure 7: Results of the OVB analysis for the recombination of two nitrogen atoms in D_{2h} symmetry using a CAS(6,6) wave function. The four CSFs are:

$$\phi_1 = p^{\alpha}_{zA}\ p^{\alpha}_{xA}\ p^{\alpha}_{yA}|p^{\beta}_{zB}\ p^{\beta}_{xB}\ p^{\beta}_{yB}$$

$$\phi_2 = p^{\alpha}_{zA}\ p^{\alpha}_{xA}\ p^{2}_{yA}|p^{\beta}_{zB}\ p^{\beta}_{xB} - p^{\alpha}_{zA}\ p^{2}_{xA}\ p^{\alpha}_{yA}|p^{\beta}_{zB}\ p^{\beta}_{yB} + p^{\alpha}_{zA}\ p^{\alpha}_{xA}|p^{\beta}_{zB}\ p^{\beta}_{xB}\ p^{2}_{yB} - p^{\alpha}_{zA}\ p^{\alpha}_{yA}|p^{\beta}_{zB}\ p^{2}_{xB}\ p^{\beta}_{yB}$$

$$\phi_3 = p^{2}_{zA}p^{\alpha}_{yA}|p^{2}_{zB}p^{\beta}_{yB} - p^{2}_{zA}p^{\alpha}_{xA}|p^{\beta}_{xB}p^{2}_{yB} + p^{2}_{xA}p^{\alpha}_{yA}|p^{2}_{zB}p^{\beta}_{yB} - p^{\alpha}_{xA}p^{2}_{yA}|p^{2}_{zB}p^{\beta}_{xB}$$

$$\phi_4 = p^{\alpha}_{zA}\ p^{\alpha}_{xA}\ p^{\beta}_{yA}|p^{\beta}_{zB}\ p^{\beta}_{xB}\ p^{\alpha}_{yB}$$

p_z is specified as the p AO in the direction of the bonding, p_x and p_y are both orthogonal to p_z.

unchanged. However, there is a local rearrangement of the electron spins. This CSF is energetically not favoured. A second neutral CSF, namely ϕ_3, and the ionic CSF ϕ_2 raise in weight at a distance of 1.5 Å. Both have a weight of nearly 20 %. Their superposition describes a spatial deformation of the charge distribution (polarization).

9.2 OVB Analysis of Three-Ring Systems

There are four alicyclic ring systems with carbon and silicon atoms as ring atoms, namely cyclopropane, cylotrisilane, silacyclopropane and disilacyclopropane. The reactions studied were the following addition reactions:

$$\mathrm{XH_2} + \mathrm{H_2Y{=}ZH_2} \longrightarrow \text{c-}\mathrm{XYZH_6}$$

XH_2 can be carbene or silylene, $H_2Y{=}ZH_2$ can be ethene, disilene or silaethene. Since all ring molecules have singlet ground states as have the doubly bonded molecules, also both XH_2 molecules must be in their lowest singlet states. For the carbene molecule having a triplet ground state, this is an excited state, whereas for silylen, this is the ground state.

Table 4 summarizes the geometry parameters of various states of carbene and silylene including their singlet-triplet splitting ΔE_{ST}. The energy difference between the total energies of the lowest singulet and the lowest triplet state of the system gives the singlet-triplet splitting. A negative value for ΔE_{ST} indicates that the triplet state is the ground state. According to the computed values for the singlet-triplet splitting of the two fragments given in Table 4, the ground state of carbene is the triplet state, while the singlet state corresponds to the ground state of silylene.

In an addition reaction only the π bond is broken, the σ bond is assumed to be unchanged. The electrons in the broken π bond can make new bonds to the XH_2 molecule, if its LP electrons are decoupled as well. The description of a broken π bond needs the bonding and the antibonding π MOs, the LP electrons can be in the s or in the p LP. These four orbitals are the active orbital space of a $CAS(4,4)$ description of the reaction. To check, whether the

Table 4: Comparision of the geometry parameters of carbene and silylene in different electronic states received with the 6-311G(d,p) basis set and the excitation from the singlet to the triplet state (ΔE_{ST}) in millihartree (mH).

	Carbene (CH_2)		**Silylene (SiH_2)**	
State Symmetry	**Bond Length (C-H) [Å]**	**Bond Angle (H-C-H) [°]**	**Bond Length (Si-H) [Å]**	**Bond Angle (H-Si-H) [°]**
$^1\mathbf{A}_1$	1.098	102.3	1.513	94.2
$^3\mathbf{B}_1$	1.070	128.6	1.474	117.2
$^1\mathbf{\Delta}$	1.056	180.0	1.447	180.0
	ΔE_{ST} [mH]		**ΔE_{ST} [mH]**	
	-16.5		30.1	

σ bond is indeed not involved in the reaction, we expanded the active space by adding the bonding and the antibonding σ orbitals of the double bond and studied the reaction with a $CAS(6,6)$ wave function. In case of a $CAS(4,4)$ treatment, the orbital configurations of the doubly bonded molecules are π^2, π^{*2}, and $\pi\pi^*$, the latter giving rise to a singlet and a triplet state. Similarly, the orbital configurations of the XH_2 molecule are s^2, p^2 and sp, giving again, a singlet and a triplet state. In both cases, one gets three singlet states and one triplet state. The triplet state derived from the sp orbital configuration has two unpaired electrons, which are ready for bond making. In the singlet state, both electrons are in different spatial orbitals but they are singlet coupled. The triplet states are therefore especially important for these reactions. But all singlet states play a certain role in the addition reaction as well.

It should be emphasised that only those elimination and addition reactions were studied, where two fragments are produced by breaking two bonds of the three-ring molecule. The other possibility would result in a cleavage of all bonds between the heavy atoms that form the ring molecule, which produces three fragments. However, this type of chemical reactions are not part of this thesis. Cyclopropane and cyclotrisilane can only undergo one reaction that describes the addition of two smaller fragments. Silacyclopropan and disilacyclopropan have both two different reaction channels, where in the one case a silylene is eliminated, while in the other case a carbene is eliminated.

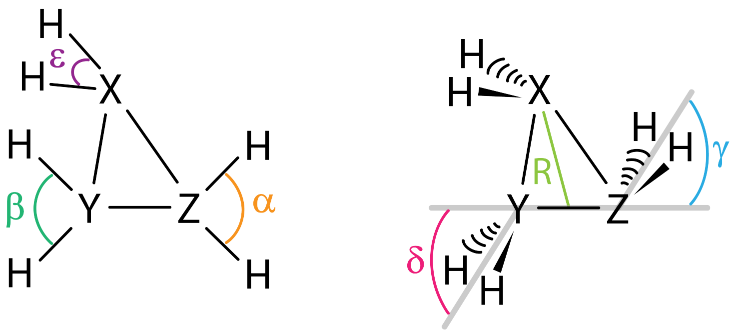

Figure 8: Definition of the bond angles (α, β, ϵ), the out-of-plane angles (γ, δ) and the reaction coordinate R for the three-ring molecules in view from above (left) abd from the side (right).

Figure 8 specifies the geometry parameter used for the description of the three-ring systems. X, Y and Z are the heavy atoms. There are a total of three important bond angles being α, β and ϵ. Moreover, the two out-of-plane angles are given by γ and δ, where γ is always assumed to be positive and δ has negative values in the case of a trans-bent structure. In a cis-bent structure both out-of-plane angles are defined to be positive. The reaction coordinate R is specified as the distance between the heavy atom X of the eliminated fragment and the midpoint of the YZ bond.

Table 5 summarizes the reaction energies as well as the energies of the barriers for all investigated three-ring systems. The reaction barriers of the products have been calculated. It is intended to give a brief overview of the computations that have been done for different reaction channels. The reaction energies for the addition reactions calculated in C_s and C_{2v} are not identical because the optimized geometries of the fragments in the dissociated molecular systems at a reaction coordinate of 5 Å are not yet identical.

Table 5: Overview of the reaction energies ΔE and the energies of the barriers $\Delta E^{\#}$ in millihartree (mH) for the addition reactions. N.c. = Not calculated, X = No reaction barrier.

	$\mathbf{C_{2v}}$				$\mathbf{C_s}$			
	CAS(4,4)		**CAS(6,6)**		**CAS(4,4)**		**CAS(6,6)**	
	ΔE	$\mathbf{\Delta E^{\#}}$	**ΔE**	$\mathbf{\Delta E^{\#}}$	**ΔE**	$\mathbf{\Delta E^{\#}}$	**ΔE**	$\mathbf{\Delta E^{\#}}$
$\mathbf{C_2H_4 + CH_2}$	-131.6	+58.1	-131.1	+59.0	-130.8	X	-130.2	X
$\mathbf{Si_2H_4 + SiH_2}$	-87.4	+30.9	-83.2	+37.1	-79.0	+33.8	-80.1	+37.5
$\mathbf{C_2H_4 + SiH_2}$	N.c.	N.c.	-39.6	+65.7	-38.5	X	-37.0	X
$\mathbf{Si_2H_4 + CH_2}$	N.c.	N.c.	-187.8	X	-164.3	X	-159.1	X
$\mathbf{SiCH_4 + CH_2}$	N.c.	N.c.	N.c.	N.c.	-159.0	X	N.c.	N.c.
$\mathbf{SiCH_4 + SiH_2}$	N.c.	N.c.	N.c.	N.c.	-76.5	X	N.c.	N.c.

9.2.1 Addition Reaction of Ethylene and Carbene to Cyclopropane in C_{2v} and C_s Symmetry

The first investigated reaction that corresponds to a three-ring system is the addition of carbene to ethylene to form cyclopropane.

$$\mathrm{C_2H_4 + CH_2 \longrightarrow c\text{-}C_3H_6}$$

The reaction has been performed in C_{2v} and C_s symmetry using a CAS(4,4) and CAS(6,6) wave function. The first part of this chapter considers the comparision of both CAS calculations with respect to C_{2v} symmetry, while the second part considers the reaction performed under C_s symmetry. Figure 9 shows that both energy curves contain a noticeably large reaction barrier at 2.5 Å, when the reaction is investigated in C_{2v} symmetry. The exclusion of the σ/σ^* orbitals of ethylene from the active space, which results in a CAS(4,4) wave function, has no influence on the shape of the PEC.

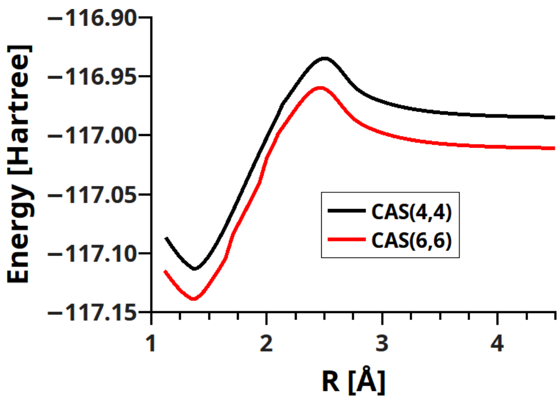

Figure 9: PECs for the addition reaction of ethylene and carbene to cyclopropane in C_{2v} symmetry using a CAS(4,4) and CAS(6,6) wave function.

Analyzing the geometry data shows clearly that the geometry parameters of the involved reactants suddenly change in a very strong manner in the

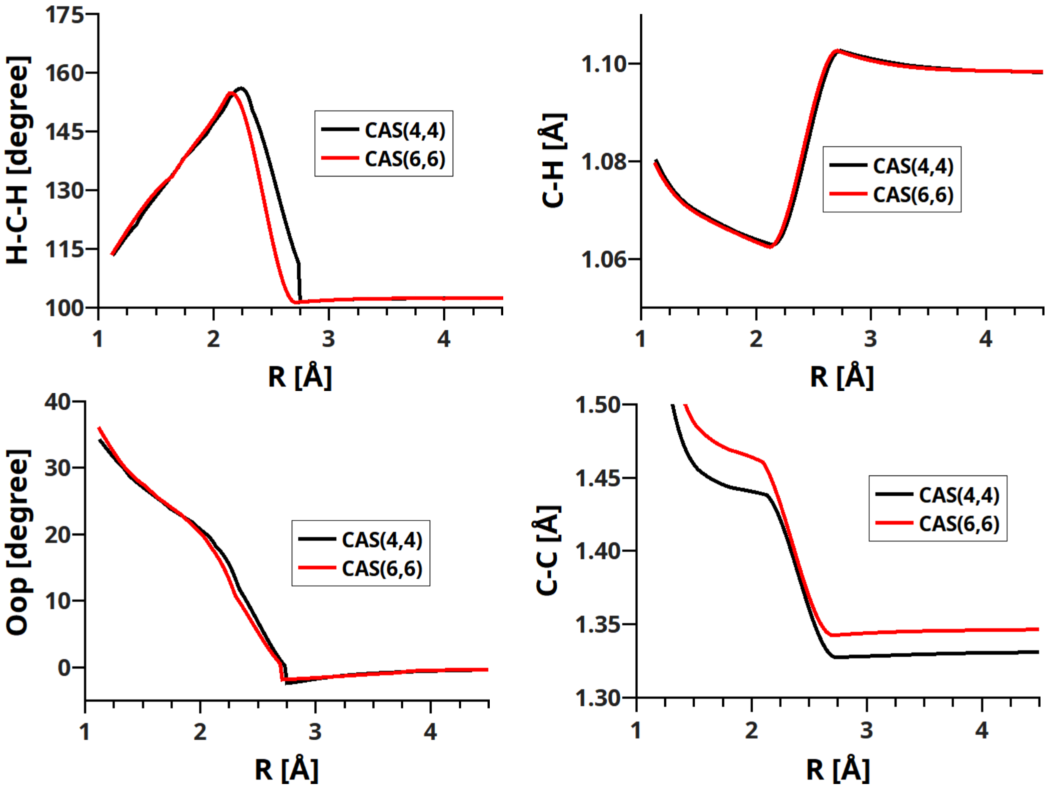

Figure 10: Bond angles and bond lengths of carbene (top) and ethylene (bottom) for the addition reaction to cyclopropane in C_{2v} symmetry using a CAS(4,4) and CAS(6,6) wave function.

interval ranging from 2.4 Å to 2.8 Å. Figure 10 shows that the bond angle in the carbene fragment increases rapidly from 102 degree to a maximum of 160 degree during the addition process. After that, the bond angle decreases to 110 degree, until the carbene molecule forms together with ethylene the final ring molecule. According to Table 4, the free carbene molecule corresponds to the singlet state, while the geometry parameters at 2.4 Å resembles the $^1\Delta$ state. At large distances the C-H bond lenght in carbene is 1.1 Å. This indicates also a state of carbene with singlet multiplicity. At a distance of 2.8 Å the C-H distance in the carbene fragment drops drastically to 1.06 Å before streching again slowly to 1.08 Å. The C-C distance in the ethylene fragment increases during the reaction from around 1.32 Å to 1.6 Å. The out-of-plane angle in ethylene drops from 35 degree to 0 degree and represents the transition from the cis-bent structure to a planar geometry.

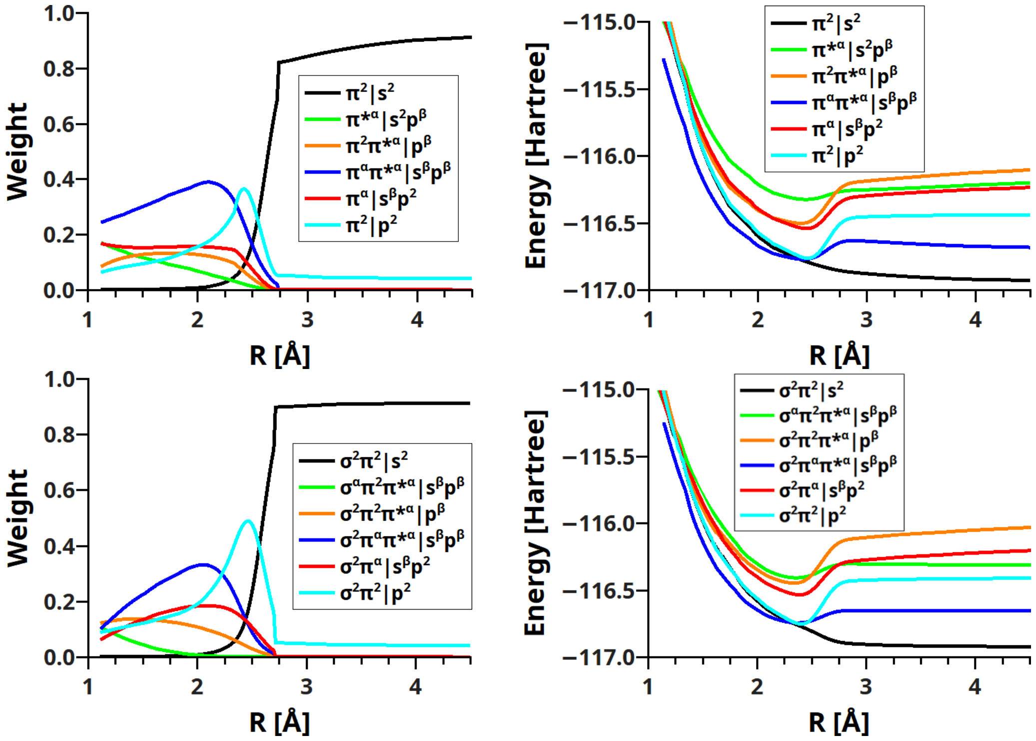

Figure 11: Results of the OVB analysis for the addition reaction of ethylene and carbene to cyclopropane in C_{2v} symmetry using a CAS(4,4) (top) and CAS(6,6) wave function (bottom).

The results of the OVB calculation in Figure 11 reveal more details about the local effects that occur during the whole reaction. Both calculations with different CAS specifications yield almost identical results. At very large distances (around 3.0 Å) between the two fragments the so-called no-bond configuration has the heighest weight with around 90 %. This CSF corresponds to the lowest doubly occupied orbitals in both fragments. The remaining 10 % belong to a CSF, where the lowest orbitals of ethylene are still doubly occupied, but the carbene fragment contains a double excitation from the s to the empty p orbital leading to its double occupation. This CSF becomes the most important one at a distance of 2.4 Å with a maximum weight of 60 %. However, it becomes more and more unimportant, when moving towards the equilibrium geometry of cyclopropane. Therefore, at 2.0 Å another CSF increases in weight and indicates a local triplet coupling in each fragment in the case of the CAS(4,4) computation. At the equilibrium state of cyclopropane two ionic CSFs start contributing. They show charge-transfer effects and electronic excitations. The ionic CSFs have at large distances between the two fragments the lowest energy, while the highest energy corresponds to the no-bond configuration. At the point, where the drastically geometry change occurs (2.4 Å), all CSFs undergo a stabilization in the energy. The only exception is the no-bond CSF, which had the highest energy up to this point and is raising in energy.

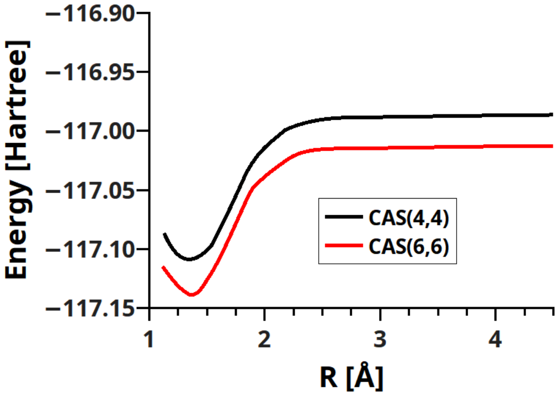

Figure 12: PECs for the addition reaction of ethylene and carbene to cyclopropane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

When the same reaction is performed using the lower symmetry group C_s, the reaction barrier disappears. It can be concluded that the reaction does not occur in C_{2v} symmetry. By comparing both PECs in Figure 12 that are obtained by using a CAS(4,4) and CAS(6,6) wave function, it can be noticed that the inclusion of the σ/σ^* orbitals of ethylene has little influence on the shape of the curve. Of course, the higher-quality wave function gives better results and leads to a shift of the curve towards lower energies.

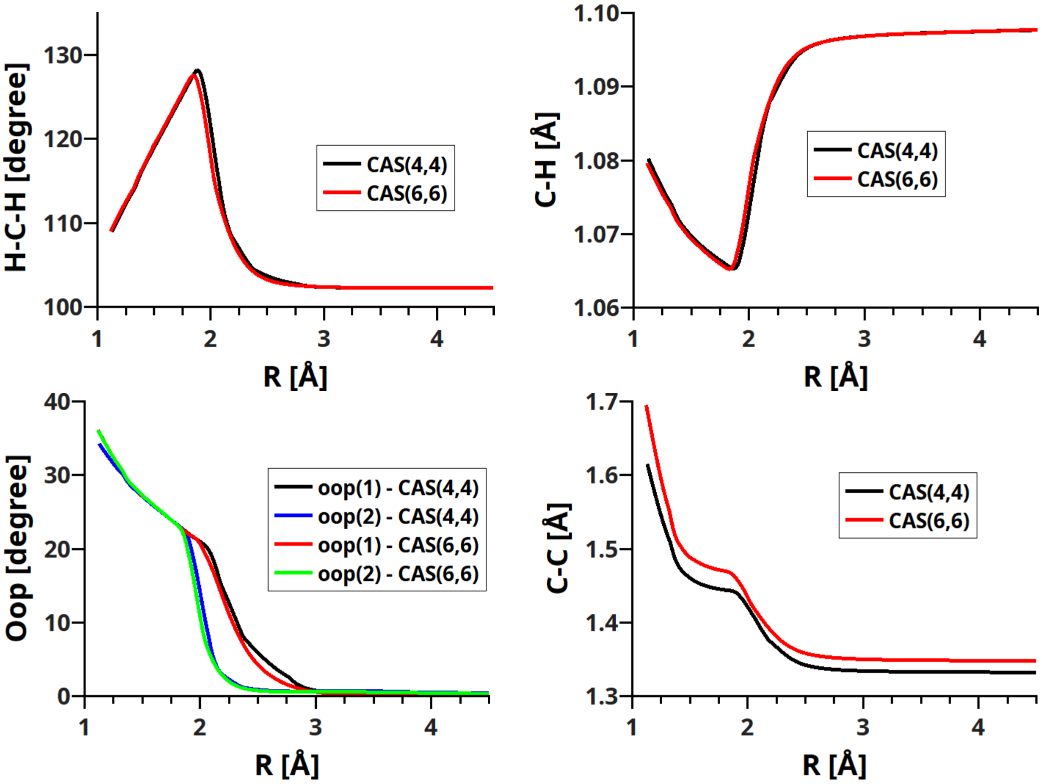

Figure 13: Bond angles and bond lengths for carbene (top) and ethylene (bottom) for the addition reaction to cyclopropane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

Figure 13 represents the geometry parameters of the addition reaction to cyclopropane in the lower C_s symmetry. The out-of-plane angle on this carbon atom is indicated by oop(1) in the plot, while oop(2) corresponds to the carbon atom, where the second bond with carbene is formed. All geometry parameters exhibit a similar behaviour compared to the reaction studied in C_{2v} symmetry with an exception of the change of the bond angle in carbene. The maximum of this bond angle is reached at a distance of 1.8 Å with a value of around 130 degree. Together with the C-H distance of 1.07 Å, it corresponds to the triplet state of carbene.

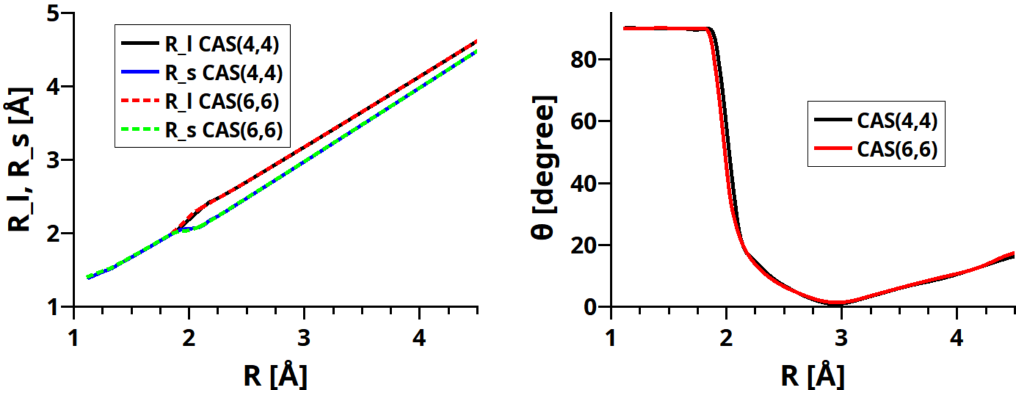

Figure 14: Distance between the carbon atoms of carbene and ethylene (left) and the deviation of carbene from planarity (right) for the addition reaction to cyclopropane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

When the symmetry gets reduced from C_{2v} to C_s, there are two additional geometry parameters that are necessary for the complete description of the addition reaction. The first graph in Figure 14 compares the two distances between the carbon atom of carbene to both carbon atoms in ethylene For both CAS specifications these two distances are inequal for large distances. This means that the carbene fragment is closer to one of the carbon atoms in ethylene (R_s = shorter distance) than to the other (R_l = longer distance) and forms the first bond to one of the carbon atoms in ethylen. At a distance of 1.8 Å both distances become equal. This means that the carbene molecule has formed the second bond to form the final ring molecule. The reaction is a two-step reaction. The graph on the right side in Figure 14 describes

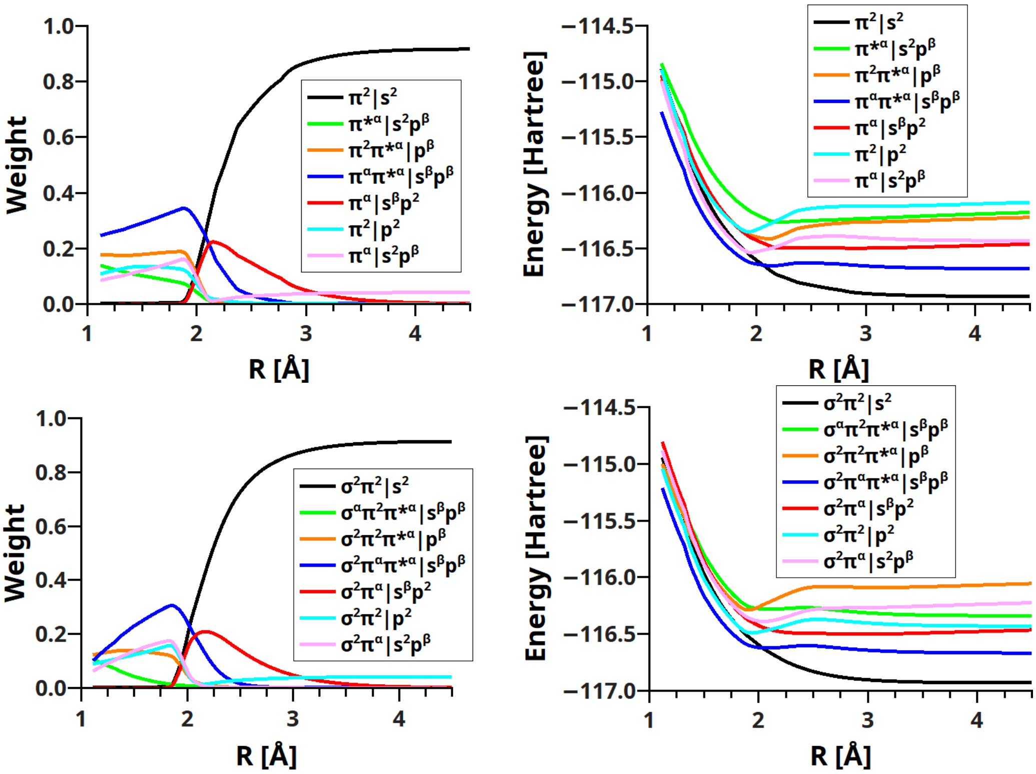

Figure 15: Results of the OVB analysis for the addition reaction of ethylene and carbene to cyclopropane in C_s symmetry using a CAS(4,4) (top) and CAS(6,6) wave function (bottom).

Analyzing the OVB calculations reveals something interesting. In C_s symmetry one additional ionic CSF appears at a distance of 2.2 Å with a maximum weight of 20 %. It corresponds to a single charge-transfer from the π orbital of ethylen to the p orbital of carbene and prepares the system for the formation of the bond. The weight reduces to zero towards equilibrium geometry. The former CSF that appeared at this point in C_{2v} symmetry has now been shifted towards shorter distances and lost about 40 % of its weight. The overall behaviour of the remaining CSFs stayed the same. The neutral and ionic ones are almost evenly weighted at the equilibrium geometry. With progressive elimination of the carbene fragment from ethylene the no-bond configuration becomes again more and more important.

9.2.2 Addition Reaction of Disilene and Silylene to Cyclotrisilane in C_{2v} and C_s Symmetry

The addition reaction of disilene and silylene to cyclotrisilane is represented by the following chemical equation:

$$Si_2H_4 + SiH_2 \longrightarrow c\text{-}Si_3H_6$$

This reaction has been studied in C_{2v} and C_s symmetry using a CAS(4,4) and CAS(6,6) wave function, analogous to cyclopropane. First of all, Figure 16 shows the PECs for the reaction investigated in C_{2v} symmetry. A very huge reaction barrier is present that takes up around one third of the stabilization energy.

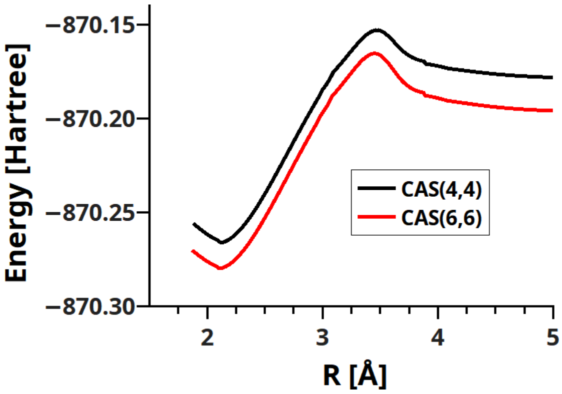

Figure 16: PECs for the addition reaction of disilene and silylene to cyclotrisilane in C_{2v} symmetry using a CAS(4,4) and CAS(6,6) wave function.

The visualization of the geometry data in Figure 17 shows a rapid change in the geometry of the fragments at a distance of 3.2 Å. The H-Si-H angle in silylene raises at first from 110 degree to 115 degree and then drastically shrinks to 93 degree in the dissociated system. The Si-H bond lenght in silylene increases from 1.474 Å to 1.514 Å. Overall, the diagrams on the top

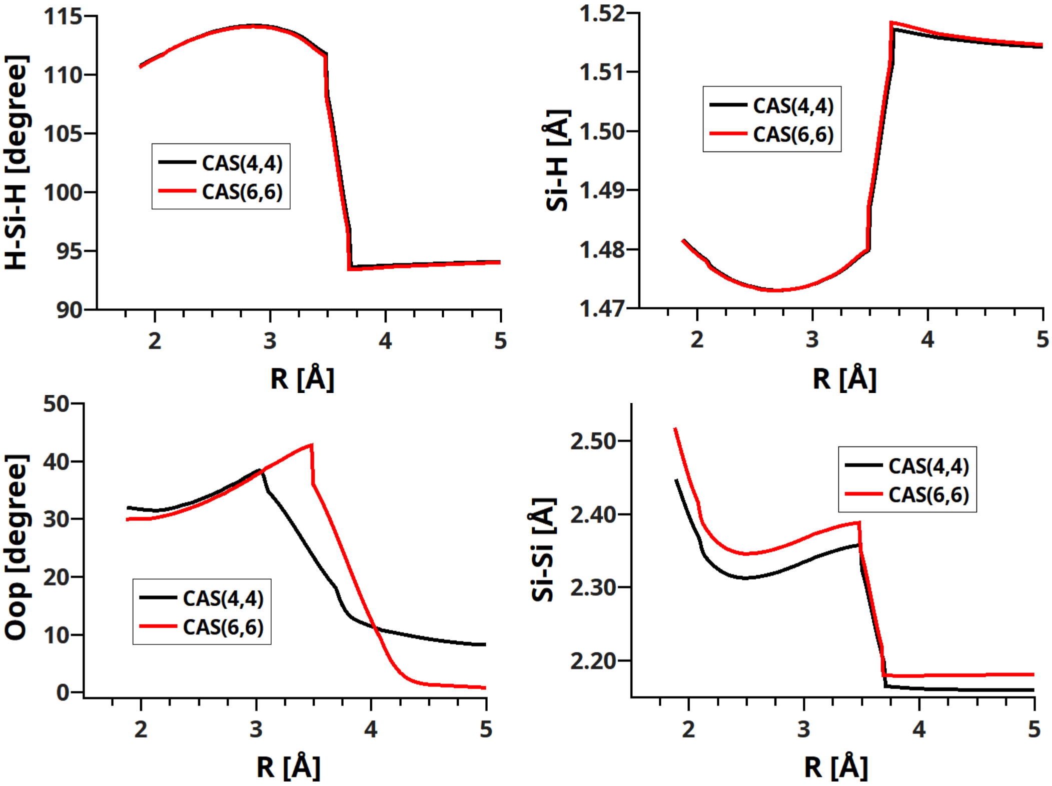

Figure 17: Bond angles and bond lengths for silylene (top) and disilene (bottom) for the addition reaction to cyclotrisilane in C_{2v} symmetry using a CAS(4,4) and CAS(6,6) wave function.

suggests that the silylene molecule changes its multiplicity from the singlet to the triplet state during the reaction. The disilene fragment in the three-ring is strongly cis-bent, the out-of-plane angle at 2.0 Å is around 30 degree. During the dissociation reaction this angle increases to about 40 degree and drops close to zero. Using C_{2v} symmetry forces the free disilene molecule to stay in a planar or slgihtly cis-bent geometry instead of its favoured trans-bent structure. The Si-Si distance in disilene increases from 2.2 Å to 2.4 Å during the elimination reaction. Figure 18 shows the results of the OVB analysis for the addition reaction of two fragments to cyclotrisilane. The weights of

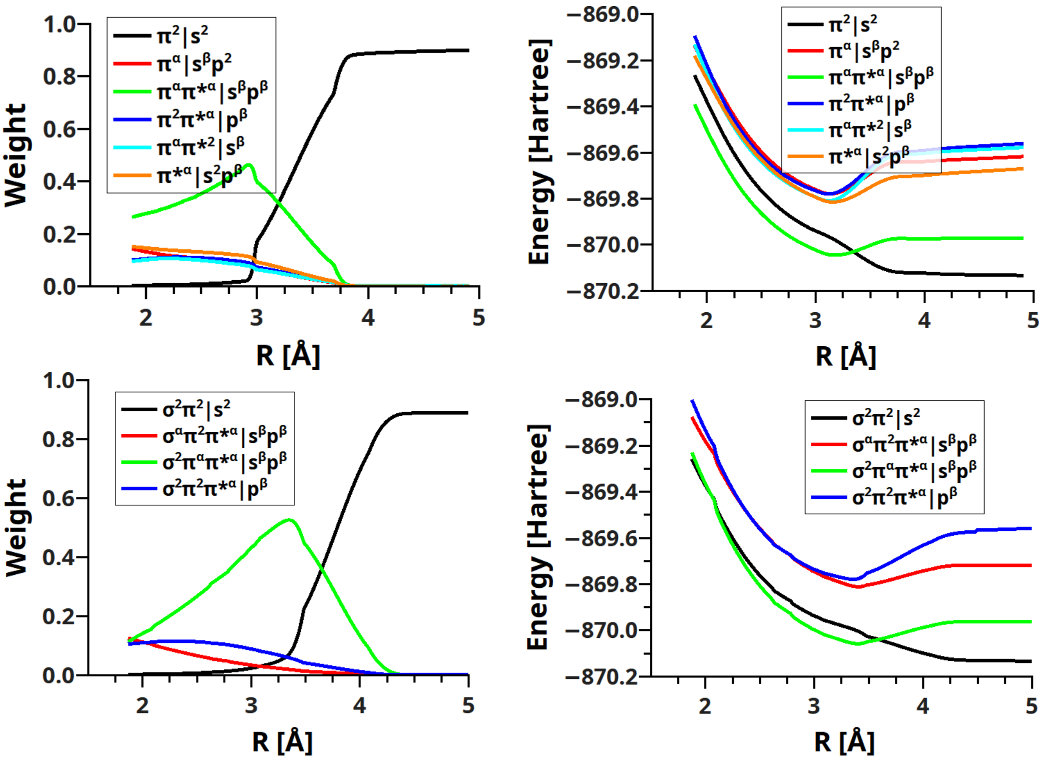

Figure 18: Results of the OVB analysis for the addition reaction of disilene and silylene to cyclotrisilane in C_{2v} symmetry using a CAS(4,4) (top) and CAS(6,6) wave function (bottom).

only four CSFs are larger than 10 % somewhere along the reaction coordinate in the case of using a CAS(6,6) wave function and are considered for an interpretation. For the same reaction without the consideration of the σ/σ^* orbitals of disilene in the active space resulting in CAS(4,4) wave function two additional CSFs become important. In the dissociated system, the non-bond CSF has a very high weight of 90 % in both CAS specifications. However, at a distance of 3.2 Å this CSF becomes entirely unimportant, while a new CSF increases in weight with a maximum of nearly 60 %. This CSF represents the coupling of two triplet states. At the equilibrium geometry of cyclotrisilane two additional ionic CSFs that describe charge-transfer effects gain weight. These CSFs are necessary to give a correct description of the covalent bonds in the three-ring molecule.

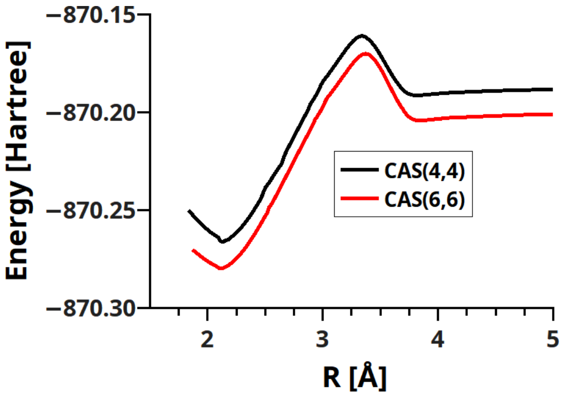

Figure 19: PECs for the addition reaction of disilene and silylene to cyclotrisilane in $\mathrm{C_s}$ symmetry using a CAS(4,4) and CAS(6,6) wave function.

Figure 19 represents the PECs for the addition reaction of disilene and silylene to cyclotrisilane in C_s symmetry. The calculated energy curves are identical to the ones that were investigated using C_{2v} symmetry. By comparing these PECs of cyclotrisilane with cyclopropane, it is noticable that the reaction barrier does not vanish, when the symmetry gets reduced to C_s. Since both CAS specifications for the reaction performed in C_{2v} and C_s symmetry yield energy curves, that are identical in terms of the location of stationary points and curvature, perfoming a CAS(4,4) calculation on the reaction of cyclotrisilane is sufficient. The σ/σ^* orbitals of disilene seem to play no decisive role in this reaction.

Figure 20 represents the geometry parameters for the reaction in C_s symmetry. While the behaviour of the silylene molecule does not change at all,

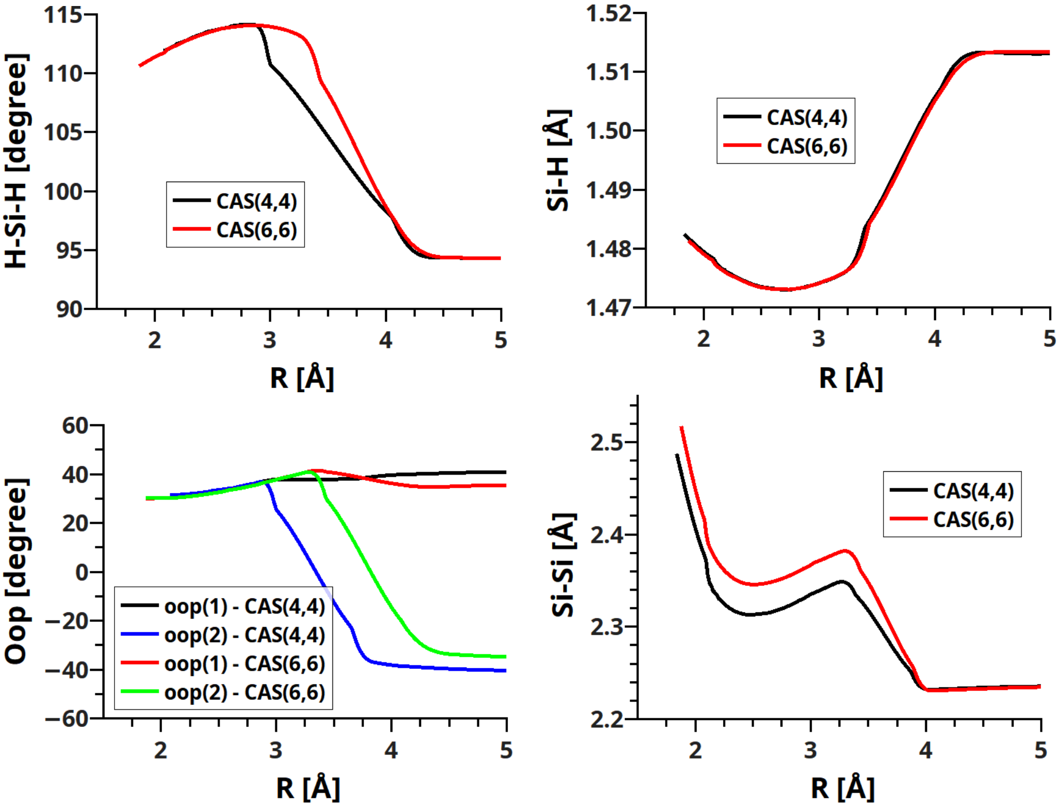

Figure 20: Bond angles and bond lengths for silylene (top) and disilene (bottom) for the addition reaction to cyclotrisilane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

the out-of-plane angles of the disilene fragment are very different from the C_{2v} reaction path. Both out-of-plane angles start to approach a value of ±35 degree at around 4.0 Å, which results in a trans-bent structure in the dissociated disilene molecule. Because of the different distances between the silylene group and and the two silicon atoms in disilene during the reaction, one of the out-of-plane angles in disilene undergoes a strong change. The out-of-plane angle oop(2) belongs to the larger distance between the heavy atoms of the two fragments and shows the biggest change. The out-of-plane angle oop(1) remains almost unvaried.

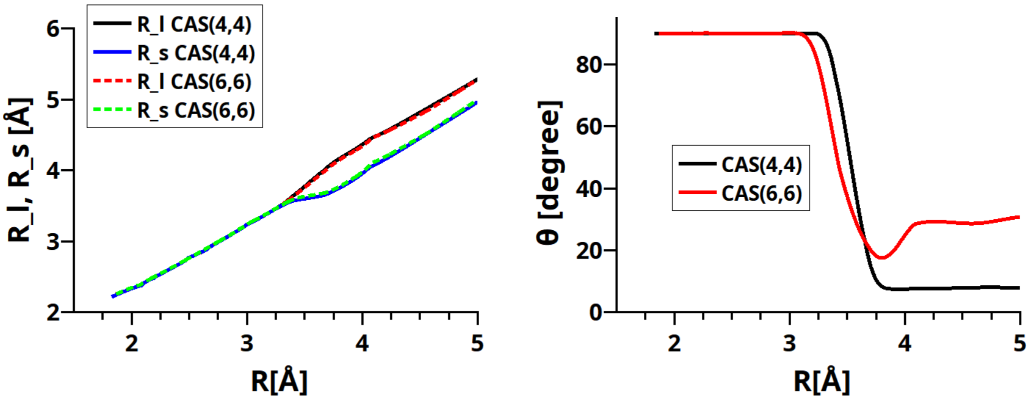

Figure 21: Distance between the silicon atoms of silylene and disilene (left) and deviation of silylene from planarity (right) for the addition reaction to cyclotrisilane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

Figure 21 contains the additional geometry parameters that are essential for the reaction studied in C_s symmetry. The graphic on the right side indicates that the addition reaction of silylene to disilen happens in two steps, analogous to the addition reaction of cyclopropane. At a distance of 3.5 Å the formation of the second bond giving the three-ring molecule is finished.

Figure 22 contains the results of the OVB analysis. In C_s symmetry only four CSFs make important contributions for the calculation using a CAS(6,6) wave function, analogous to C_{2v}. There is no significant difference between the OVB analysis of the different symmetries. All four dominant CSsF contain a doubly occupied σ orbital and an unoccupied σ^* orbital. Only the π/π^* orbitals are variable occupied. Using a CAS(4,4) wave function for the OVB analyis in C_s symmetry yields a total of seven CSF that play an important role.

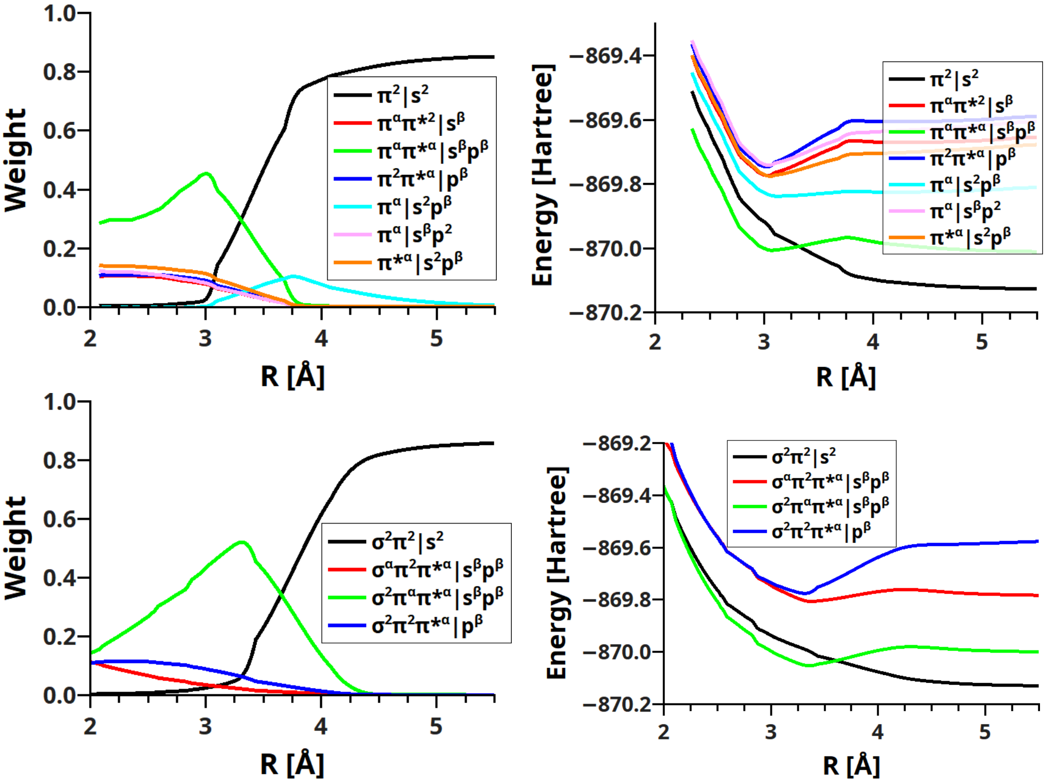

Figure 22: Results of the OVB analysis for the addition reaction of disilene and silylene to cyclotrisilane in C_s symmetry using a CAS(4,4) (top) and CAS(6,6) wave function (bottom).

9.2.3 Addition Reaction of Ethylene and Silylene to Silacyclopropane in C_{2v} and C_s Symmetry

There are two possible reaction channels named with $R1$ and $R2$ for the addition of two fragments to form silacyclopropane.

$$R1\text{: } C_2H_4 + SiH_2 \longrightarrow \text{c-}SiC_2H_6$$
$$R2\text{: } SiCH_4 + CH_2 \longrightarrow \text{c-}SiC_2H_6$$

While the first reaction channel $R1$ is described in this section, $R2$ will be discussed in a separate part of this thesis. The PEC of $R1$ in Figure 23 shows that the addition reaction of ethylene and silylene to silacyclopropane in C_{2v} symmetry has a high barrier. Figure 24 represents the geometry data of both fragments. There is a sudden change in the geometry parameters in the region between 2.4 Å and 2.8 Å. After the angle of silylene has increased, it decreases strongly. The final bond angle of silylene is 94 degree, which corresponds to the singlet ground-state of this molecule. Moreover, the Si-H bond length gets streched from 1.47 Å to 1.52 Å. This behaviour

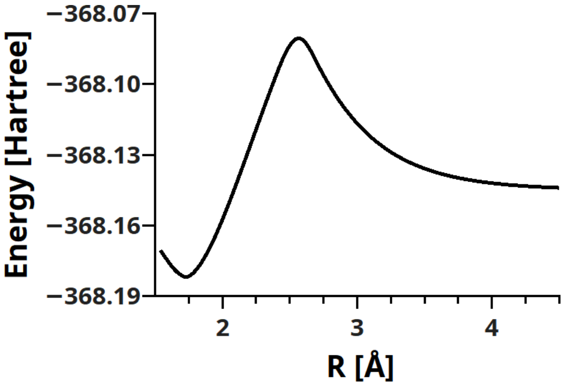

Figure 23: PEC for the addition reaction of ethylene and silylene to silacyclopropane in C_{2v} symmetry using a CAS(6,6) wave function.

indicates also a transition from the triplet to the singlet state of silylene. The out-of-plane-angle of ethylene decreases linearly starting at 40 degree until it reaches the completely planar structure. Furthermore, the C-C distance shortens from 1.6 Å to 1.35 Å.

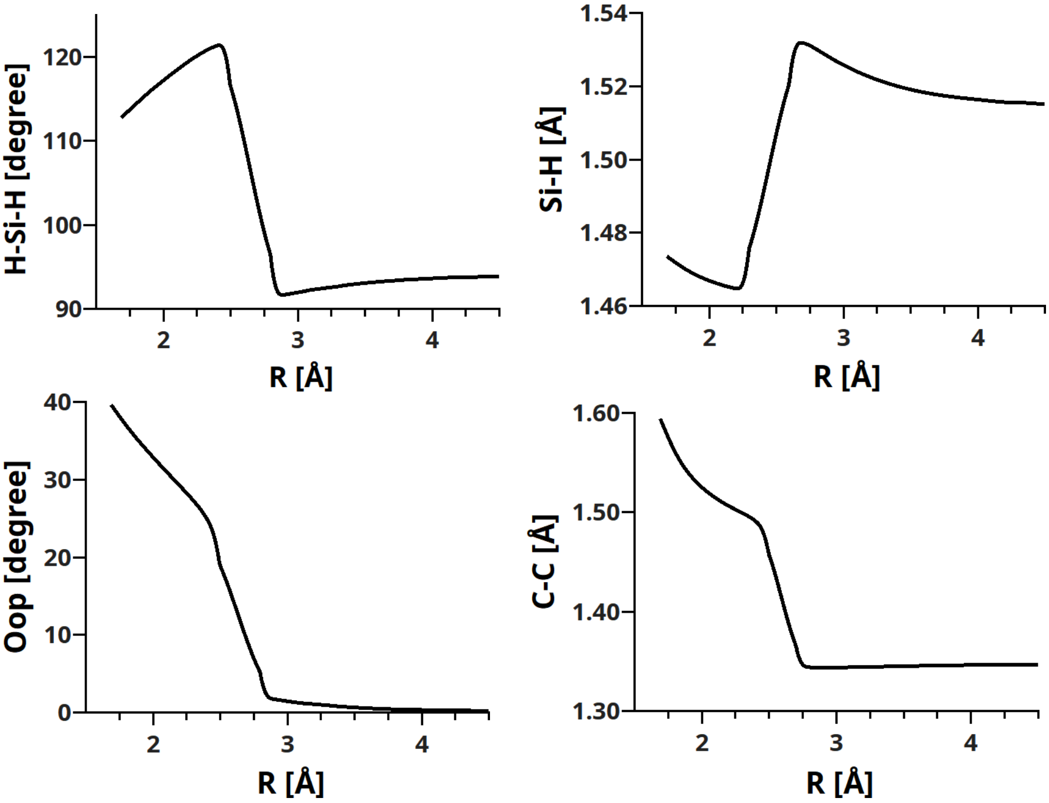

Figure 24: Bond angles and bond lengths for silylene (top) and ethylene (bottom) for the addition reaction to silacyclopropane in C_{2v} symmetry using a CAS(6,6) wave function.

The results of the OVB analysis in Figure 25 yield a total of six important CSFs. Compared to theaddition reactions of cyclopropane and cyclotrisilane in C_{2v} symmetry using a $CAS(6,6)$ wave function, it is recognizable that the number and types of CSFs of silacyclopropane matches best with cyclopropane. However, minor differences in their weights can be spotted. The CSF, where the lowest MOs of ethylene as well as the p orbital of silylene are doubly occupied, has a maximum weight of 20 % at a distance of 2.5 Å. In comparision to cyclopropane this CSF has lost about two third of its weight. The maximum weight of the CSF that describes the local triplet coupling in the two fragments has a value of 35 %. All CSFs with an exception of the no-bond CSF experience a stabilization in their energy at approximately a distance of 2.6 Å.

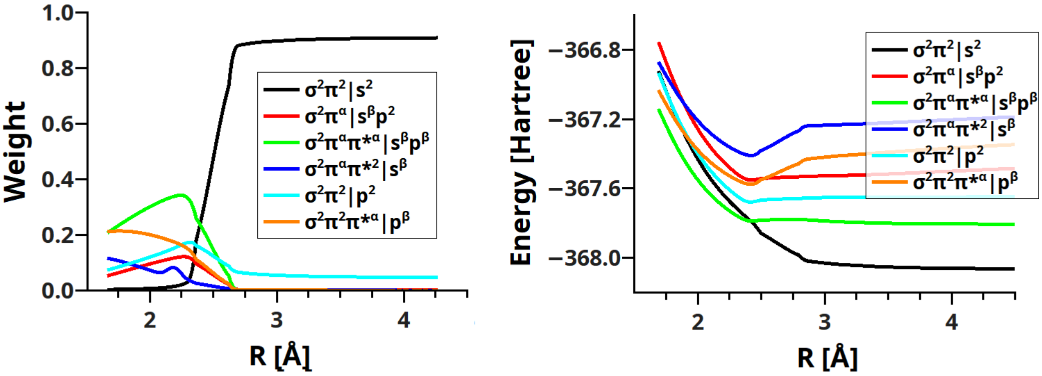

Figure 25: Results of the OVB analysis for the addition reaction of ethylene and silylene to silacyclopropane in C_{2v} symmetry using a CAS(6,6) wave function.

When the addition reaction $R1$ is performed using the lower point group C_s, the reaction barrier vanishes. Figure 26 shows the computed PEC. This means that the reaction is strongly hindered in C_{2v} symmetry. If the deformation of the fragments in C_s becomes allowed, the reaction barrier disappears. Therefore, the chemical reaction is only correctly described by this symmetry group. The inclusion of the σ/σ^* orbitals of ethylene are not inevitably necessary for the correct description of this reaction, since the calculation with the higher-quality wave function has no significant influence on the shape of the energy curve.

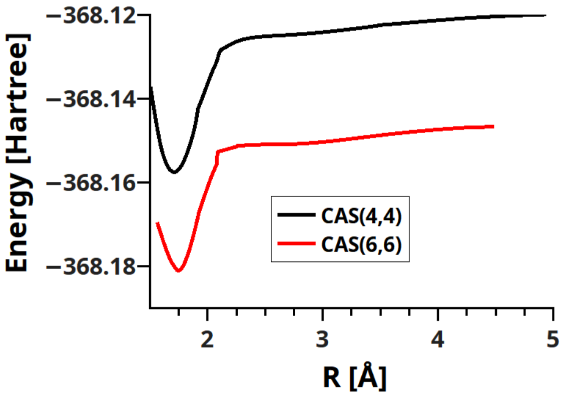

Figure 26: PEC for the addition reaction of ethylene and silylene to silacyclopropane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

The change of the geometry parameters in C_s symmetry in Figure 27 is very similar to C_{2v} symmetry. First, silylene starts to approach the planar ethylene molecule. At a distance of around 2.6 Å the out-of-plane angle oop(1) begins to deviate from zero. This out-of-plane angle belongs to the CH_2 group in ethylene that interacts and forms the first bond with the silylene molecule. When the distance of 2.0 Å is reached, the second bond between the two fragments forms leading to the three-ring structure. This is indicated by a strong increase of the H-Si-H bond angle in silylene, as well as by the sudden change of the second out-of-plane angle oop(2).

The first graph in Figure 28 shows that there is indeed a two-step mechanism involved. Both OVB analysis in Figure 29 belonging to the two different CAS specifications yield a total of seven important CSFs. Using the $CAS(6,6)$ specification leaves the σ orbital of ethylene always double occupied for all

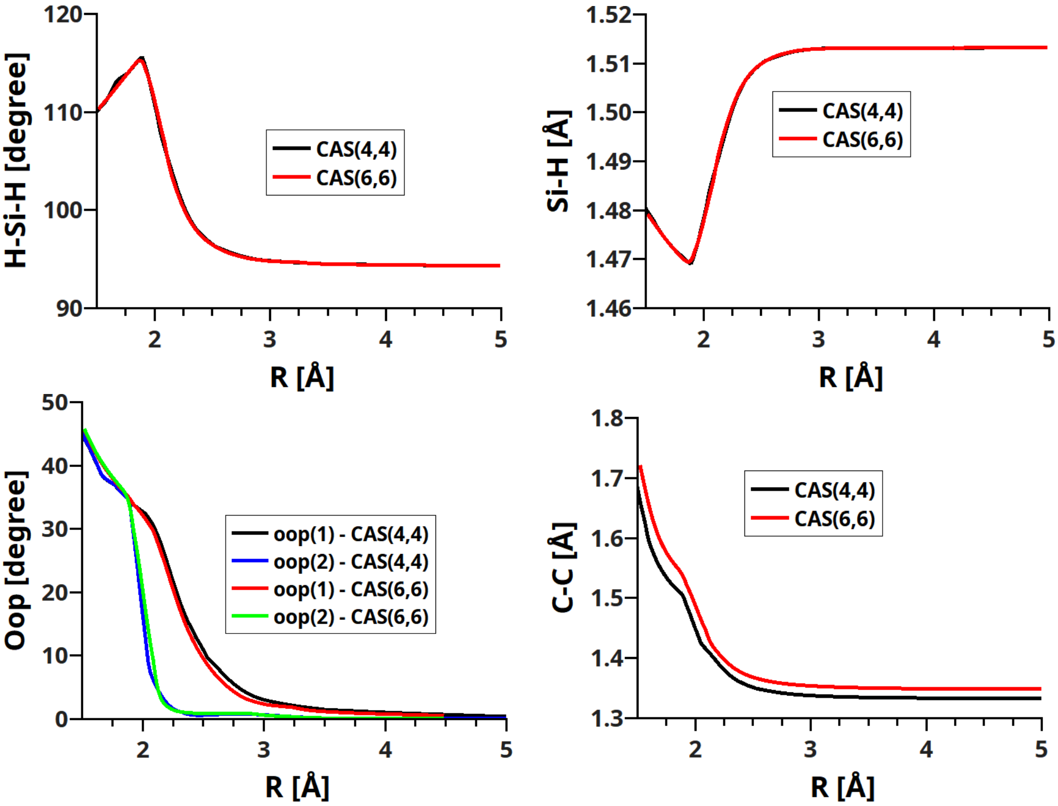

Figure 27: Bond angles and bond lengths for silylene (top) and ethylene (bottom) for the addition reaction to silacyclopropane in in C$_s$ symmetry using a CAS(4,4) and CAS(6,6) wave function.

CSFs. If this orbital is neglected, six of the seven CSFs match exactly with the ones of the lower-quality $CAS(4,4)$ wave function. Moreover, the change of their weights over the whole reaction coordinate is also identical. One CSF differs in both cases. The CSF for the $CAS(6,6)$ wave function having the p orbital of silylene doubly occupied has a very low weight of 15 %. Furthermore, the maximum value of this CSF in C_s symmetry is shifted toward shorter distances compared to C_{2v} symmetry. Using a $CAS(4,4)$ wave function replaces this CSF with one that leaves only the π/π^* orbitals of ethylene

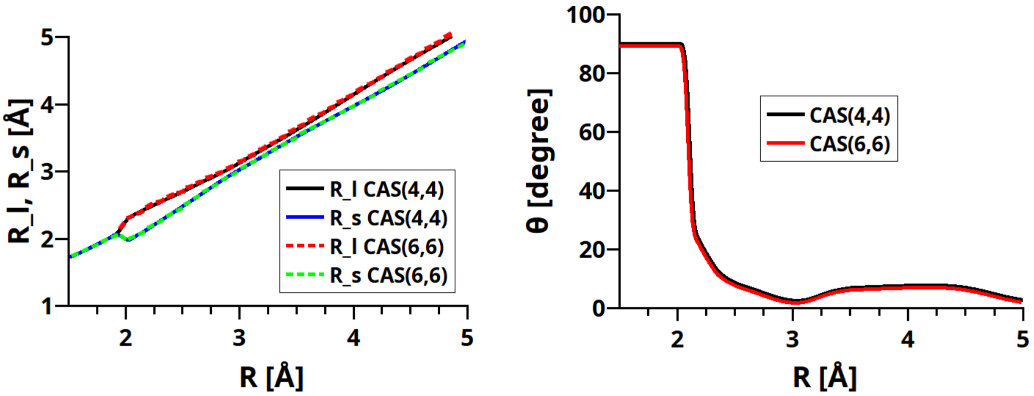

Figure 28: Distance between the silicon atom of silylene and the carbon atoms of ethylene (left) and the deviation of silylene from planarity (right) for the addition reaction to silacyclopropane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

doubly occupied, which has by far the heighest energy at a distance of 2.0 Å.

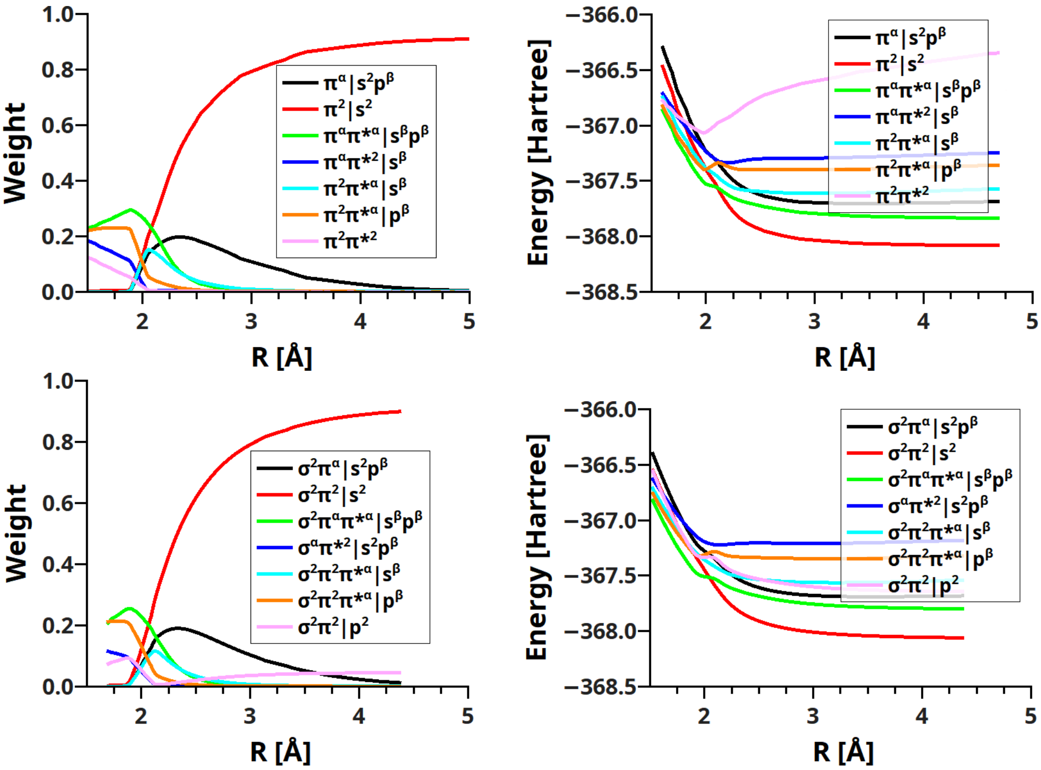

Figure 29: Results of the OVB analysis for the addition reaction of ethylene and silylene to silacyclopropane in C_s symmetry using a CAS(4,4) (top) and a CAS(6,6) wave function (bottom).

9.2.4 Addition Reaction of Disilene and Carbene to Disilacyclopropane in C_{2v} and C_s Symmetry

As for silacyclopropane, there are also two possibilities for the addition reaction to disilacylcopropane that invlove two reactants.

$$R3\text{: } \mathrm{Si_2H_4} + \mathrm{CH_2} \longrightarrow \text{c-}\mathrm{Si_2CH_6}$$
$$R4\text{: } \mathrm{SiCH_4} + \mathrm{SiH_2} \longrightarrow \text{c-}\mathrm{Si_2CH_6}$$

The reaction channel $R3$ describes the addition reaction of disilene and carbene to disilacyclopropane and is discussed in the recent chapter. The other reaction $R4$ recombines silaethene with silylene to form the three-ring molecule. However, this reaction is investigated in another chapter of this thesis. Figure 30 illustrates the PECs that correspond to the reaction $R3$ using C_{2v} symmetry. Interestingly, the computed energy curve does not contain any reaction barrier. The interpretation of the geometry parameters in Figure 31 leads to the assumption that the dissociated carbene molecule is in its triplet ground state. As the carbene fragment gets closer to disilene,

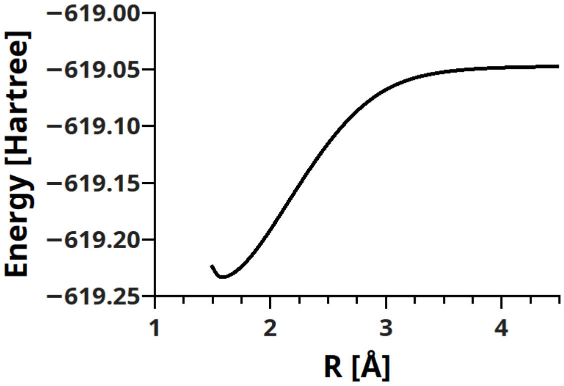

Figure 30: PEC for the addition reaction of disilene and carbene to disilacyclopropane in C_{2v} symmetry using a CAS(6,6) wave function.

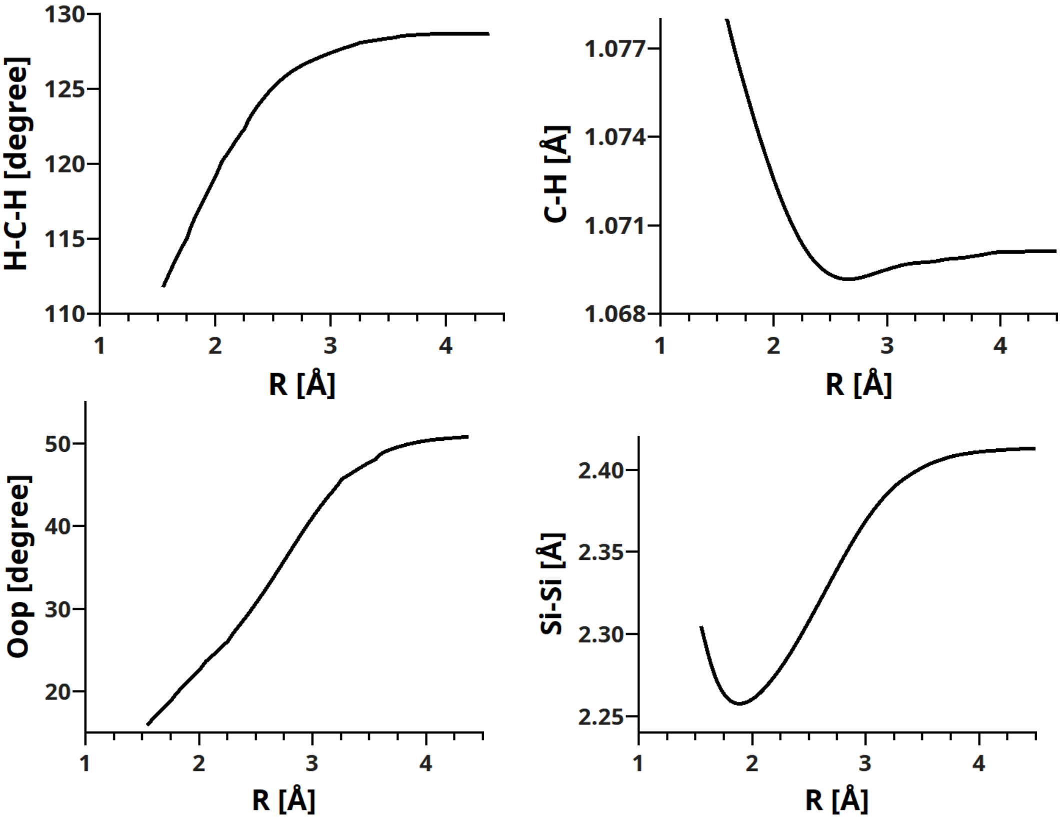

Figure 31: Bond angles and bond lengths for carbene (top) and disilene (bottom) for the addition reaction to disilacyclopropane in C_{2v} symmetry using a CAS(6,6) wave function.

the H-C-H angle of carbene decreases continuously from 128 degree to 112 degree, while the C-H distance streches from 1.070 Å to 1.078 Å. At large distances, the disilene fragment has a cis-bent structure with an out-of-plane angle of around 50 degree. The value of the out-of-plane angle decreases to 18 degree during the addition reaction. Moreover, the Si-Si bond lenght in the free disilene molecule is 2.42 Å and gets reduced to 2.26 Å at a distance of 1.8 Å between the two fragments. At this distance the Si-Si distance reaches a minimum and the bond formation begins. After that, the distance between the two silicon atoms increase again to 2.3 Å.

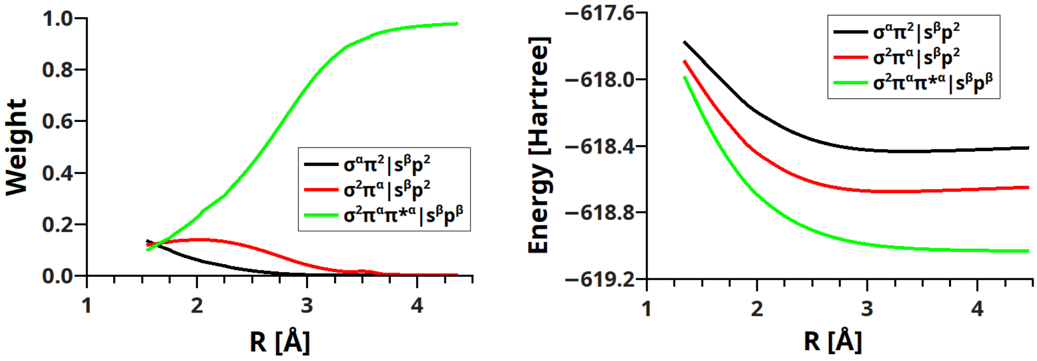

Figure 32: Results of the OVB analysis for the addition reaction of disilene and carbene to disilacyclopropane in C_{2v} symmetry using a CAS(6,6) wave function.

The OVB analysis in Figure 32 belongs to the the addition reaction to silacyclopropane according to $R3$ in C_{2v} symmetry with a CAS(6,6) wave function. Only three CSFs resulted in weights over 10 % somewhere along the reaction coordinate R and thus were important enough for an interpretation. At the equilibrium geometry all three CSFs are evenly weighted having a 10 % share. One CSF is neutral and the other two are ionic. At the dissociation limit, the CSF that describes a local triplet coupling in the two fragments increases strongly in its weight up to 100 %. The assumption that at large distances both fragments are present in their respective triplet states is confirmed.

Figure 33 represents the calculated PECs for the reaction $R3$ under C_s symmetry. There are no reaction barriers present analogous to the reaction studied in C_{2v} symmetry. However, under the reduction of the point group to C_s two hidden processes become visible. Up to the distance of 3.1 Å, the

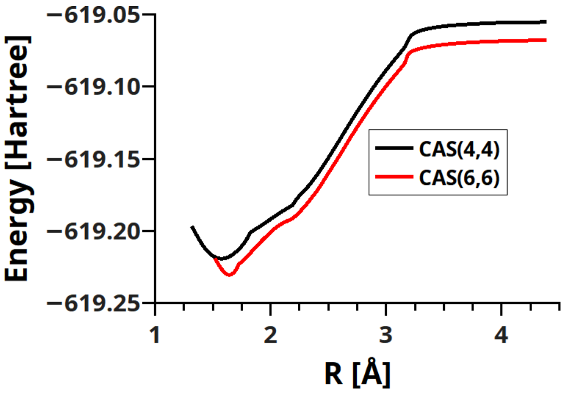

Figure 33: PECs for the addition reaction of disilene and carbene to disilacyclopropane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

fragments are far enough away from each other that there is yet no interaction between them and the fully dissociation limit is reached. In the interval of 2.2 and 3.1 Å something rather strange seems to happen. Both PECs show a linear dependency of the reaction coordinate. This can be explained with the reorganization by the roatation of the not yet bound reactants. All investigated geometry parameters in Figure 34 do not change significantly in this interval and are almost constant. The first bond formation of carbene to one of the silicon atoms in disilene happens at a distance of 2.1 Å and leads to a small stabilization in the total energy of the system. The final stabilization through the bond formation of the second Si-C bond is obsverved at a distance of 1.8 Å. If there are more electrons that can be distributed among the orbitals of disilene, the effect of the stabilization due to bond formation is more visible.

The geometry parameters for the addition reaction $R3$ in C_s symmetry are given in Figure 34. In comparison to the higher C_{2v} symmetry, the H-C-H

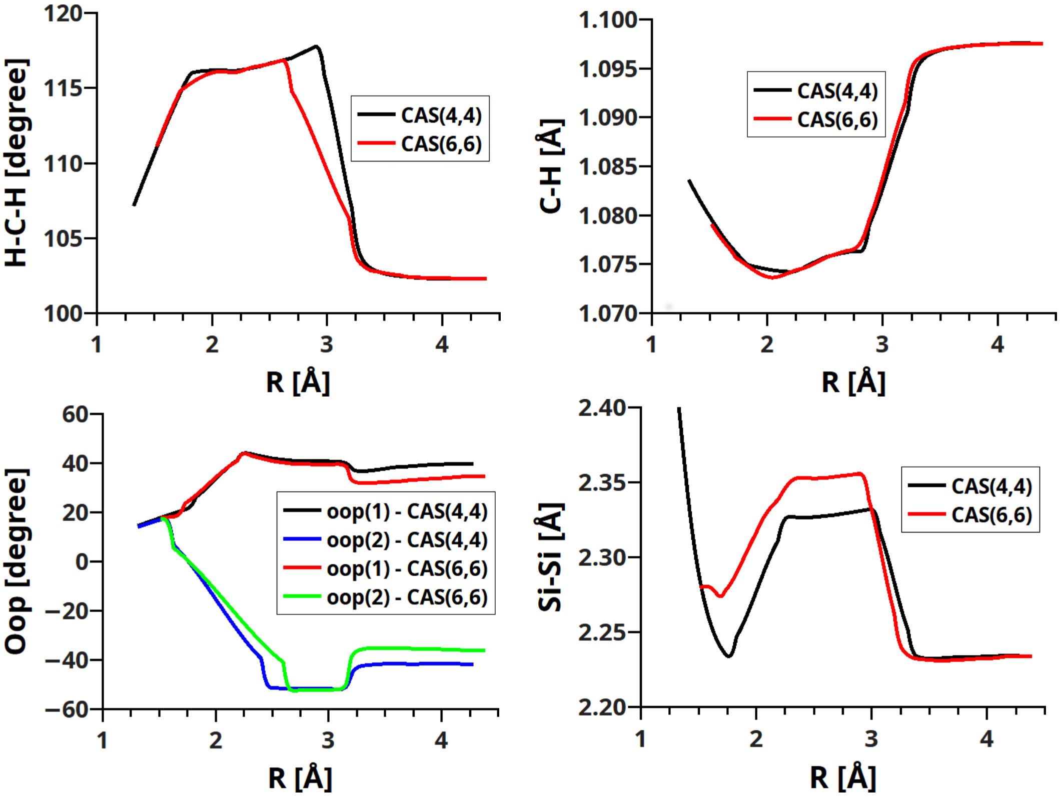

Figure 34: Bond angles and bond lengths for carbene (top) and disilene (bottom) for the addition reaction to disilacyclopropane in C_s symmetry using a CAS(4,4) and CAS(6,6) wave function.

angle of 102 degree and the C-H lenght of 1.098 Å of the dissociated carbene fragment, resembles a singlet state. Moreover, the out-of-plane angles of disilene have different signs and indicate a trans-bent structure. This explains the difference in the reaction energies in Table 5, when the reaction is performed in different symmetry groups. The trans-bent structure of disilene is energetically favoured compared to the cis form.

Figure 36 contains the results of the OVB analysis of the addition reaction

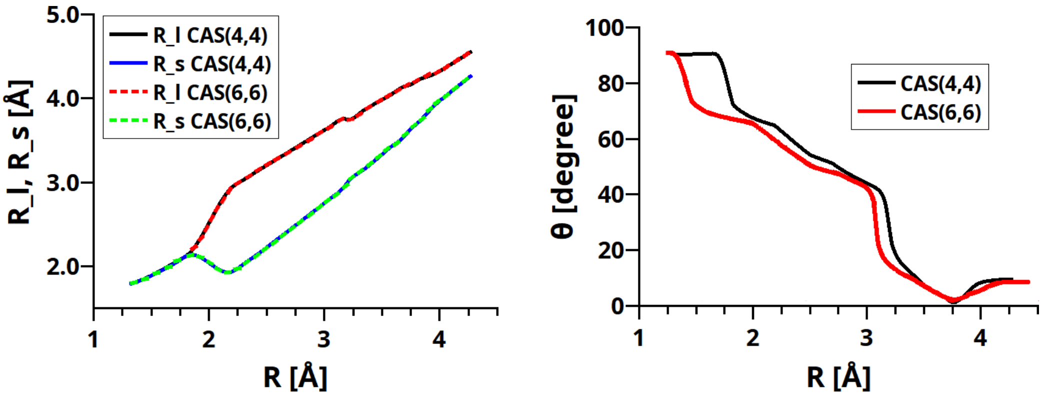

Figure 35: Distance between the carbon atom of carbene and the silicon atoms of disilene (left) and the deviation of carbene from planarity (right) for the addition reaction to disilacyclopropane in $\mathrm{C_s}$ symmetry using a CAS(4,4) and CAS(6,6) wave function.

of disilene and carbene to silacyclopropane in C_s symmetry. The no-bond CSF, where the electrons occupy the lowest orbitals of the fragments, appears at large distances awith a weight of nearly 90 %. This configuration has been absent in the OVB analysis of silacyclopropane using the higher C_{2v} symmetry. At a distance of 3.2 Å, where the interaction between carbene and disilene starts to play a role, a local triplet coupling happens in both CAS specifications. Moreover, at this distance all CSFs with exception to the no-bond CSF undergo a stabilization in their total energies.

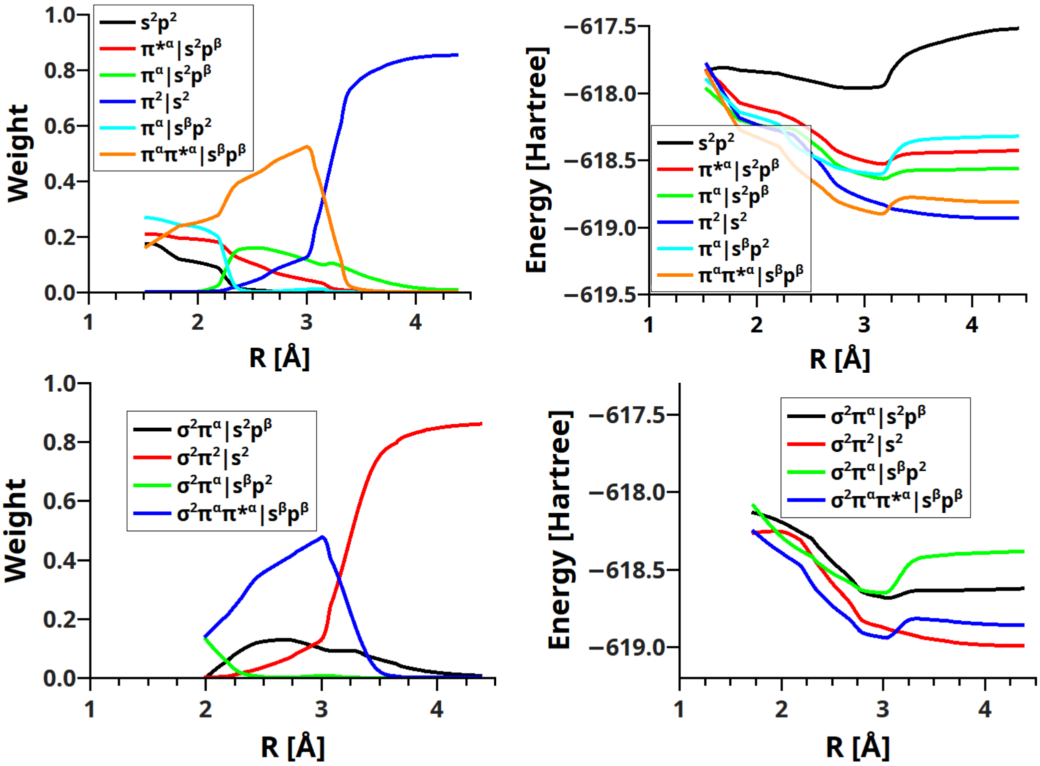

Figure 36: Results of the OVB analysis for the addition reaction of disilene and carbene to disilacyclopropane in C_s symmetry using a CAS(4,4) (top) and a CAS(6,6) wave function (bottom).

9.2.5 Addition Reaction of Silaethene and Carbene to Silacyclopropane in C_s Symmetry

The last two chapters of this thesis investigates the addition reaction of a carbene-like fragment to a double-bonded molecule that contains two inequal heavy atoms. The addition reaction of a carbene fragment to silaethene leads to silacyclopropane and was investigated in C_s symmetry using a $CAS(4,4)$ wavefunction. This means that the σ/σ^* orbitals from silaethene are not included in the active space. This reaction was only investigated in C_s symmetry, because the reaction is not possible in C_2 symmetry due to the missing two-fold rotation axis and vertical mirror plane.

$$\mathrm{SiCH_4} + \mathrm{CH_2} \longrightarrow \text{c-}\mathrm{SiC_2H_6}$$

The shape of the calculated PEC in Figure 37 indicates a two-step mechanism.

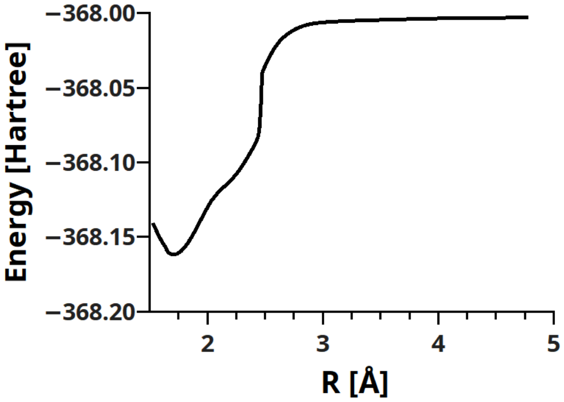

Figure 37: PEC for the addition reaction of silaethene and carbene to silacyclopropane in C_s symmetry using a CAS(4,4) wave function.

The interpretation of the geometry parameters in Figure 38 gives insight into this phenomenon. Silaethene has a trans-bent structure at large distances.

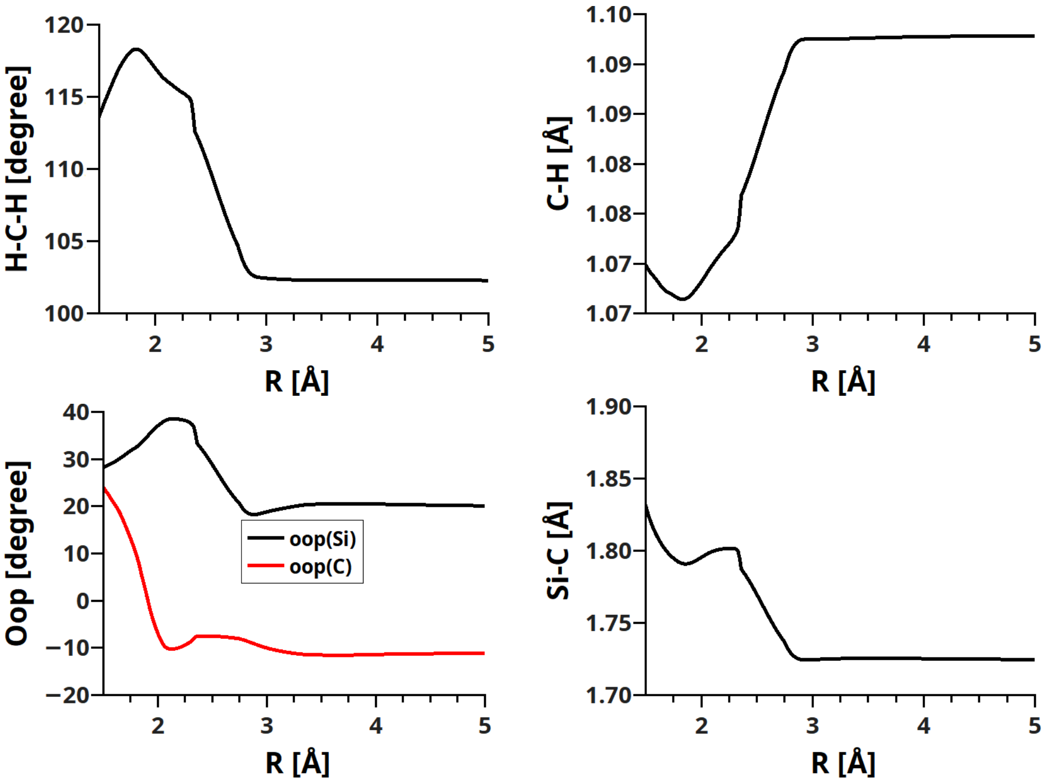

Figure 38: Bond angles and bond lengths of carbene and silaethene for the addition reaction to silacyclopropane in C_s symmetry using a CAS(4,4) wave function.

The interaction between the two fragments starts at a distance of 2.6 Å. Although the C-C bond is about 2.5 kJ/mol[1] stronger than the Si-C bond, the carbene molecule prefers to form the first bond with the silicon atom of silaethene. This preference for the bond formation can be explained due to the bigger size of the silicon atoms compared to carbon. When the carbene fragment gets closer to the silaethene molecule, it will first feel the interaction caused by the bigger silicon atom. The first bond formation is indicated

---

[1] The bond strenghts have been calculated with the MCSCF method using a CAS(2,2) wave function and the basis set 6-311G(d,p).

by a strong and rapid stabilization in the PEC at a distance of 2.2 Å. At this distance the out-of-plane angle on the silicon atom increases from 20 to 40 degree. Moreover, the distance between the heavy atoms in silaethene becomes longer at the same time. At a distance of 1.8 Å the second bond between carbene and the carbon atom of silaethene that leads to the three-ring is formed. There is a less rapid stabilization in in the energy curve that finally leads to the minimum. The out-of-plane angle that corresponds to the CH_2 group of silaethene changes in a very strong manner from -10 degree up to 30 degree. The other out-of-plane angle belongs to the SiH_2 group of silaethene and has always positive values. This menas that there is a transition from the trans- to the cis-bent form of silaethene during the reaction.

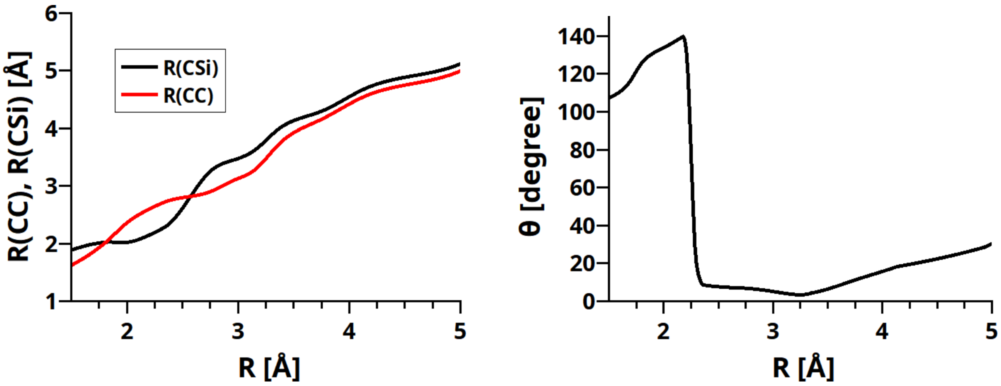

Figure 39: Distance between the carbon atom of carbene and the heavy atoms of silaethene (left) and the deviation of carbene from planarity (right) for the addition reaction to silacyclopropane in C_s symmetry using a CAS(4,4) wave function.

Figure 40 represents the results of the OVB analysis. In the non-bonded state the no-bond CSF has the heighest weight of 90 %. At a distance of 3.0 Å an ionic CSF becomes important that describes the electron transfer from

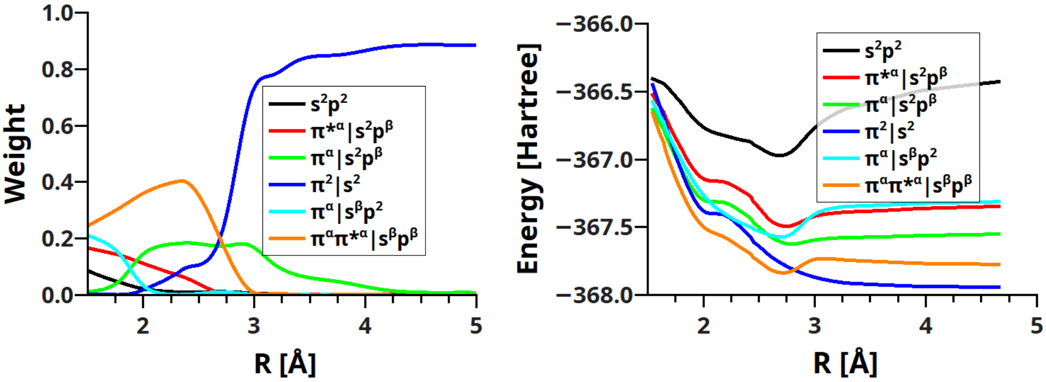

Figure 40: Results of the OVB analysis for the addition reaction of silaethene and carbene to silacyclopropane in C_s symmetry using a CAS(4,4) wave function.

the π orbital of silaethene to the p orbital of carbene. This ionic CSF has a weight of 20 % and in between 2.0 Å and 3.0 Å. The CSF that indicates a local triplet coupling in the two fragments reaches its maximum weight of over 40 % at a distance of 2.4 Å.

9.2.6 Addition Reaction of Silaethene and Silylene to Disilacyclopropane in C_s Symmetry

The second reaction that leads to disilacyclopropane as a product is the addition of silylene to silaethene.

$$\mathrm{SiCH_4} + \mathrm{SiH_2} \longrightarrow \text{c-}\mathrm{Si_2CH_6}$$

The reaction was investigated in C_s symmetry using a $CAS(4,4)$ wave function. Figure 41 shows the PEC of this reaction. There is no reaction barrier and the shape of the curve proposes a two-step mechanism. Contrary to expectation, the approaching silylene molecule prefers the formation of the first bond with silicon rather than with carbon. This is unexpected because the bond strenght of a Si-C single bond has a value of 386 kJ/mol and is a lot stronger than the single bond between two silicon atoms, which has only a energy of 262 kJ/mol.[2] However, the preference for the bond formation

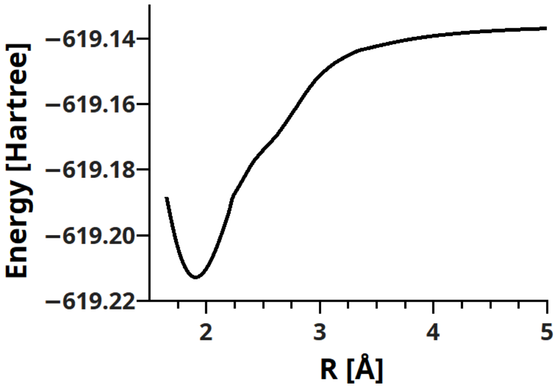

Figure 41: PEC for the addition reaction of silaethene and silylene to disilacyclopropane in C_s symmetry using a CAS(4,4) wave function.

---

[2] The bond strenghts have been calculated with the MCSCF method using a CAS(2,2) wave function and the basis set 6-311G(d,p).

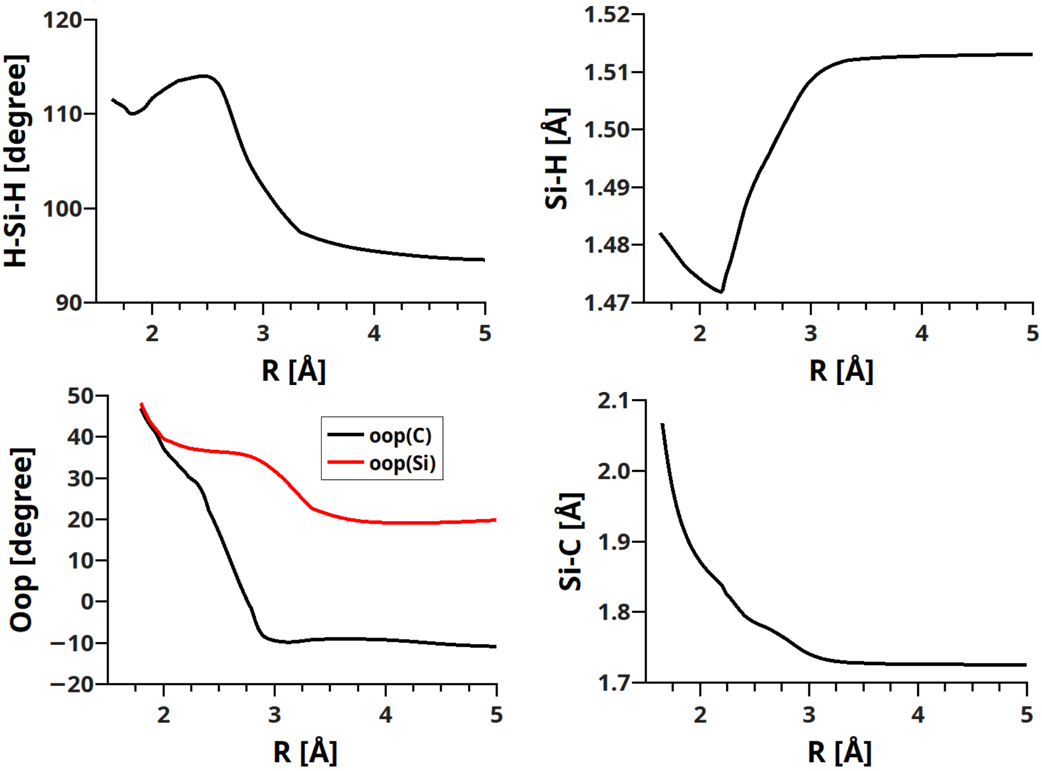

Figure 42: Bond angles and bond lengths of silylene and silaethene for the addition reaction to disilacyclopropane in C_s symmetry using a CAS(4,4) wave function.

between these two silicon atoms can be explained due to the bigger size of the silicon atoms compared to carbon. When the silylene molecule approaches towards the silaethene molecule, it begins to feel the interaction caused by the bigger silicon atom. Because of this interaction, the fragment starts to move into the direction of the silicon atom and forms the weaker Si-Si bond first. At large distances the silaethene fragment has a trans-bent structure with a Si-C distance of 1.72 Å. The geometry parameters of the dissociated silylene molecule belong to the singlet state.

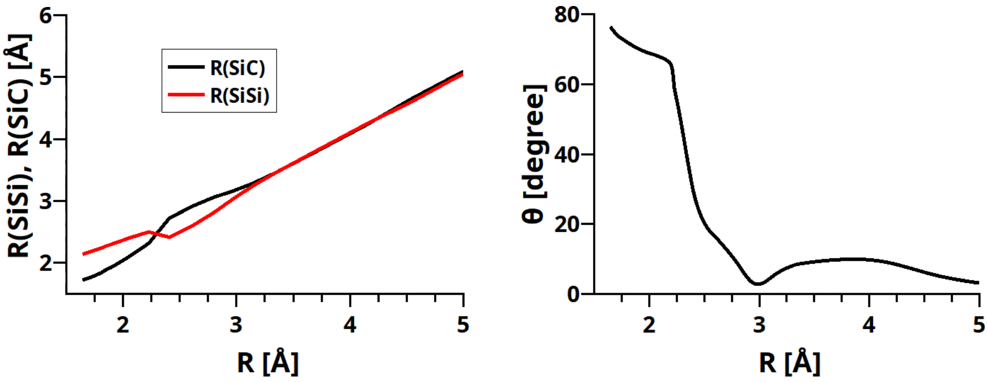

Figure 43: Distance between the silicon atom of silylene and the heavy atoms of silaethene (left) and the deviation of silylene from planarity (right) for the addition reaction to disilacyclopropane in C_s symmetry using a CAS(4,4) wave function.

The interpretation of the OVB analyis in Figure 44 is analogous to the addition reaction of silaethene and carbene.

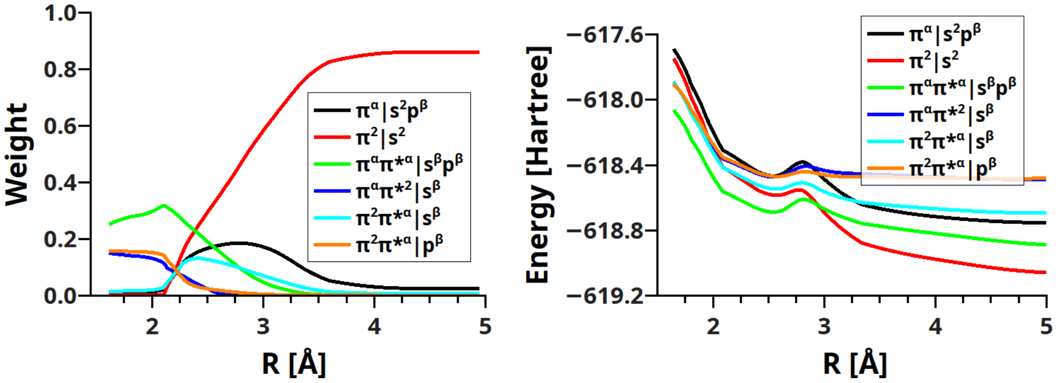

Figure 44: Results of the OVB analysis for the addition reaction of silaethene and silylene to disilacyclopropane in C_s symmetry using a CAS(4,4) wave function.

10 Computational Details

The 6-311G(d,p) triple-zeta basis set has been used to perform all computations throughout this work.[22] This kind of basis set contains polarization functions which are important to receive reasonable molecular structures and energies. The selected step size for the geometry optimizations was 0.05 Å. At larger distances the increment was increased to 0.1 Å and finally raised to 0.2 Å. The coordinate referred to as the reaction coordinate of the heavy atoms has been frozen during the optimization process. Moreover, the calculations of the optimization have been carried out in the symmetry that was indicated in each case. Last but not least, a modified version of GAMESS[23] has been used that includes the program for the generation of the localized orbitals (FOs).

11 Conclusion

According to Lewis, two atoms sharing an electron pair are held together by a covalent bond, each atom contributes one electron. For atoms connected by a single bond, each atom must be a radical having an unpaired electron. Heitler and London showed that the stabilizing electron pair is formed by one α and one β electron coupled to a singlet spin state. Accordingly, two atoms can form two covalent bonds, if each atom contributes two unpaired electrons and this means they must be in a triplet high-spin state. A triple bond can be formed, if each atom contributes three unpaired electrons in a quartet high-spin state. If the conditions for Hund's rule are fulfilled, namely, that the orbitals occupied by the unpaired electrons are energetically degenerate or nearly degenerate, then the high-spin state is always energetically favored. This holds exactly for the nitrogen atom (^4S ground state), where three electrons occupy the three degenerate p AOs and for the imidogen radical ($^3\Sigma$ ground state) with two electrons in the doubly degenerate π orbitals. It holds only approximately for non-linear carbene ($^3B_1$ ground state) because the two LP orbitals are not degenerate but have rather similar orbital energies. For silylene, the energetic difference between both LP AOs is very large and therefore the lower s-type AO is doubly occupied. To make silylene ready for bond making, an excitation from the singlet ground state into the lowest excited triplet state is necessary.

Since all dissociation and elimination reactions were studied for molecules in singlet ground states, also the fragments must be coupled to an overall singlet state. This is automatically fulfilled in case of the dissociation of the dinitrogen molecule and of diimide, where both fragments are equal and in high spin ground states. These dissociations are easy to describe because the

CSF describing the coupling of the high-spin ground states of the fragments to a singlet dominates the whole reaction. The situation is different in case of the elimination reactions. All doubly bonded fragments have singlet ground states and high lying triplet excited states, silylene has also a singlet ground state and a high lying triplet, but carbene has a triplet ground state and a not too high lying excited triplet. Therefore, in all carbene elimination reactions the carbene is not in its ground state but in its excited singlet state. For the reverse addition reaction, where both reacting molecules must be transferred into high spin states to be prepared for bond making. For the carbene, this is an de-excitation and therefore does not cost energy but yields a stabilization energy, while for the doubly bonded molecules, it is always an excitation and costs energy. The total energy needed for the preparation of both reacting molecules is therefore directly proportional to the singlet-triplet excitation energy of the doubly bonded molecules. For elimination of silylene or in the reverse addition reactions, both fragments must be excited into higher lying triplet states, which is costly. That during the reaction fragments change from low- to high-spin states is reflected by the changes in the geometry parameters of the involved molecular species. The OVB analysis shows indeed corresponding changes when a fragment changes from a high-spin to a low-spin state and vice versa.

The elimination reactions allow also to discuss the role of orbital symmetry in these reactions. From the six studied reactions, four can occur in high $C_{2\mathrm{v}}$ symmetry and in low C_{s} symmetry, the remaining two reactions occur only in low C_{s} symmetry. Orbital symmetry considerations of chemical reactions (Woodward-Hoffmann rules) explains the occurrence of large reaction barriers by correlation of the active orbitals. If for a given overall symmetry an occupied reactant orbital of a certain IRREP correlates with a virtual product orbital of the same IRREP and vice versa, then the reaction is forbidden due to orbital symmetry and a large reaction barrier will occur. If however due to a reduction of the overall symmetry reactant and product orbitals belong to the same IRREP, then the reaction is symmetry allowed and the barrier will be reduced or disappears completely. What orbital symmetry cannot explain is the reason for high or low reaction barriers.

OVB analysis shows the following: In high symmetry several ionic LFO CSFs have zero weight, that means polarization represented by these CSFs is not possible. Only local excitation to high-spin states prepares the system for bond making. In low symmetry, however, these ionic CSFs are symmetry allowed and they describe asymmetric deformations of the electron distribution, and these deformations are less costly than the local excitations. So the combination of asymmetric deformation and local excitation is energetically favored over pure excitation without asymmetric deformation. Local excitation and atomic polarization are intrinsic atomic properties, knowing properties of one system does not mean that one knows another one completely, every new system can provide a surprise. But it should not be a surprise that local effects dominate the stabilization of molecular systems, that means chemical bonding.

A final comment to the energetic stabilization of three-ring molecules. All molecules are thermodynamically stable, for all addition reactions but the addition of silylene to disilene the reaction barrier disappears, when the symmetry is lowered from $C_{2\mathrm{v}}$ to C_{s}, and to get a rough thermodynamic estimate of the reaction energies one must consider that for all reactions involving carbene the reaction energies must be reduced by the singlet-triplet splitting. Considering that both cyclotrisilane and disilene were listed as nonexistent compounds for a long time, the high stability of cyclotrisilane against thermodynamic decomposition was surprising.[24] OVB analysis shows that the similar values of the reaction energies for the elimination of carbene from cyclopropane and of silylene from cyclotrisilane, where the reaction barrier must be considered, are caused by different local processes causing different geometric changes of the reacting fragments.

Bibliography

[1] R. D. Levine. *Molecular Reaction Dynamics.* Cambridge University Press, 2005.

[2] B. O. Roos. *The Complete Active Space Self-Consistent Field Method and its Applications in Electronic Structure Calculations.* Adv. Chem. Phys. 69, 399-445 (1987).

[3] B. O. Roos. *Lecture Notes in Quantum Chemistry.* Berlin: Springer, 1992, p. 177-254.

[4] K. Ruedenberg and K. R. Sundberg. *Quantum Science.* Plenum, 1976, p. 505-515.

[5] K. Ruedenberg, K. R. Sundberg and L. M. Cheung. *Dimerization of Carbene to Ethylene.* J. Am. Chem. Soc. 100, 8024-8025 (1978).

[6] K. Ruedenberg, K. R. Sundberg and L. M. Cheung. *Electronic Rearrangements During Chemical Reactions II. Planar Dissociation of Ethylene.* Int. J. Quantum Chem. 16, 1003-1039 (1979).

[7] K. Ruedenberg, M. W. Schmidt., M. Gilbert and S. T. Elbert. *Are atoms intrinsic to molecular electronic wave functions? I The FORS model.* Chem. Phys. 71, 41-49 (1982).

[8] K. Ruedenberg, M. W. Schmidt., M. Gilbert and S. T. Elbert. *Are atoms intrinsic to molecular electronic wave functions? II Analysis of FORS orbitals.* Chem. Phys. 71, 51-64 (1982).

[9] K. Ruedenberg, M. W. Schmidt., M. Gilbert and S. T. Elbert. *Are atoms intrinsic to molecular electronic wave functions? III Analysis of FORS configurations.* Chem. Phys. 71, 65-78 (1982).

[10] D. F. Feller, M. W. Schmidt and K. Ruedenberg. *Concerted Dihydrogen Exchange between Ethane and Ethylene. SCF and FORS Calculations of the Barrier*. J. Am. Chem. Soc. 104, 960-967 (1982).

[11] Alexander F. Sax. *Localization of Molecular Orbitals on Fragments.* Journal of Computational Chemistry 33, 1495-1510 (2012).

[12] Alexander F. Sax. *Chemical Bonding: The Orthogonal Valence-Bond View.* Int. J. Mol. Sci. 16, 8896-8933 (2015).

[13] Alexander F. Sax. *OVB analysis of symmetry allowed and symmetry forbidden chemical reactions.* Comput. Theor. Chem. 1116, 117-133 (2015).

[14] Roy McWeeny. *Methods of Molecular Quantum Mechanics*, Academic Press, Second edition.

[15] I. Shavitt. *Methods of Electronic Structure Theory*, Wiley-VCH, 1977 p. 189-276.

[16] Christopher J. Cramer. *Essentials of Computational Chemistry: Theories and Models.* Wiley, 2017, Second edition, p. 208.

[17] S. Shaik. and P. C. Hilberty. *A Chemist's Guide to Valence Bond Theory.* Wiley-Interscience, 2008, p. 58-60.

[18] S. Shaik. *What happens to Molecules as they react?.* J. Am. Chem. Soc. 103, 3692-3701 (1981).

[19] F. L. Pilar. *Elementary Quantum Chemistry.* McGraw-Hill, 1968.

[20] G. H. Golub and C. F. van Loan. *Matrix Computations.* The Johns Hopkins University Press, 1996.

[21] Lionel Salem. *Electrons in Chemical Reactions: First Principles.* John Wiley & Sons, 1982, p. 28-32.

[22] Frank Jensen. *Introduction to Computational Chemistry.* Wiley & Sons, 2007, Second edition.

[23] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery. *GAMESS.* J. Comput. Chem. 14, 1347-1363 (1993).

[24] A. Masamune, Y. Hanzawam, S. Murakami, T. Baily and J. F. Blount. *Cyclotrisilane* (R_2Si)$_3$ *and Disilene* ($R_2Si{=}SiR_2$) *Systems: Synthesis and Characterization.* J. Am. Chem. Soc. 104, 1150-1153 (1982).

[25] L. Piela. *Ideas of Quantum Chemistry.* Elsevier, 2014.

A Appendix

A.1 Shorthand Notation for the Slater Determinant

A Slater determinant is defined in the following way[14]:

$$\Psi^{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \dots & \chi_N(N) \end{vmatrix}$$

The prefactor $\frac{1}{\sqrt{N!}}$ ensures normalization. The total number of electrons is given by N, while the one-electron orbitals are described by χ. It is possible to abbreviate this notation. An example of this shorthand form will be shown on a system that has two electrons and two orbitals. The orbitals are named with a and b.

$$|ab| = \frac{1}{\sqrt{2!}} \begin{vmatrix} a(1) & b(1) \\ a(2) & b(2) \end{vmatrix} = \frac{1}{\sqrt{2}}(a(1)b(2) - b(1)a(2)) = \frac{1}{\sqrt{2}}(ab - ba)$$

The row index represents the electron number and the index of the column corresponds to the number of the orbital.

A.2 Performing Symmetry Operations on Molecules, AOs and MOs

If a symmetry operation is performed on a molecule, it is also important to know how the AOs (single-electron wave functions) transform under this operation. First of all, a specification of the coordinate system that contains the molecule is necessary. Performing the symmetry operations of the point group C_{2v} that include $\hat{E}$ (identity element), $\hat{C}_2$ (rotation about an axis by 180 degree), $\hat{\sigma}_{xz}$ and $\hat{\sigma}_{yz}$ (reflections on mirror planes) on the molecule in Figure 45 leads to the following result:

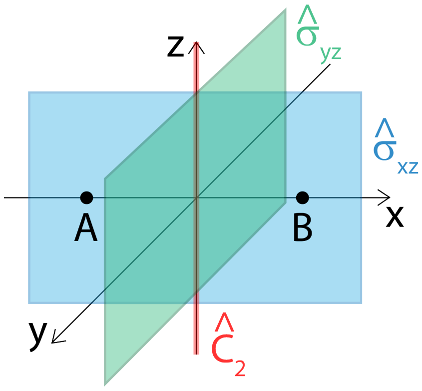

Figure 45: Definition of the positions of two symmetry equivalent atoms A and B including the two-fold rotation axis and both mirror planes of the point group C_{2v}.

$$\begin{aligned} \hat{E}A &= A & \hat{E}B &= B \\ \hat{C}_2A &= B & \hat{C}_2B &= A \\ \hat{\sigma}_{xz}A &= A & \hat{\sigma}_{xz}B &= B \\ \hat{\sigma}_{yz}A &= B & \hat{\sigma}_{yz}B &= A \end{aligned}$$

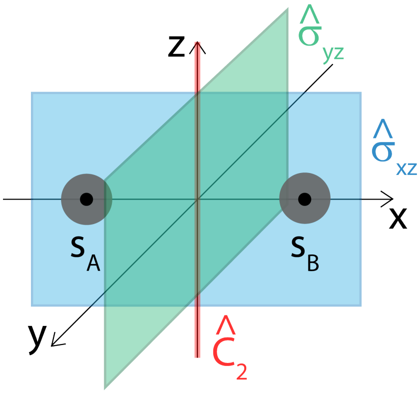

Figure 46: Adding of the respective s AOs on the atoms A and B.

Table 6: Summary of the transformation behaviour of the localized AOs under the symmetry operations of the point group C_{2v}.

$\hat{\mathbf{E}}$	$\hat{\mathbf{C}}_\mathbf{2}$	$\hat{\sigma}_{\mathbf{xz}}$	$\hat{\sigma}_{\mathbf{yz}}$
s_A	s_B	s_A	s_B
p_{Az}	p_{Bz}	p_{Az}	p_{Bz}
p'_{Az}	$-p'_{Bz}$	p'_{Az}	$-p'_{Bz}$
p_{Ax}	p_{Bx}	p_{Ax}	p_{Bx}
p'_{Ax}	$-p'_{Bx}$	p'_{Ax}	$-p'_{Bx}$

Now, the same symmetry operations of the point group C_{2v} can be performed on the s and p AOs on atom A given in Figure 46 and Figure 47. This leads to the results presented in Table 6, where p indicates the in-phase AOs and p' indicates the out-of-phase AOs. Finally, the MOs (many-electron wave functions) will be considered that describe a double bond (σ, σ^*, π and π^*). A general symmetry operator $\hat{O}$ acts in the following way on the many-electron wave function Ψ built from the single-electron wave functions ψ:

$$\hat{O}\Psi(\psi_1, \psi_2, ..., \psi_n) = \Psi(\hat{O}\psi_1, \hat{O}\psi_2, ..., \hat{O}\psi_n) \tag{15}$$

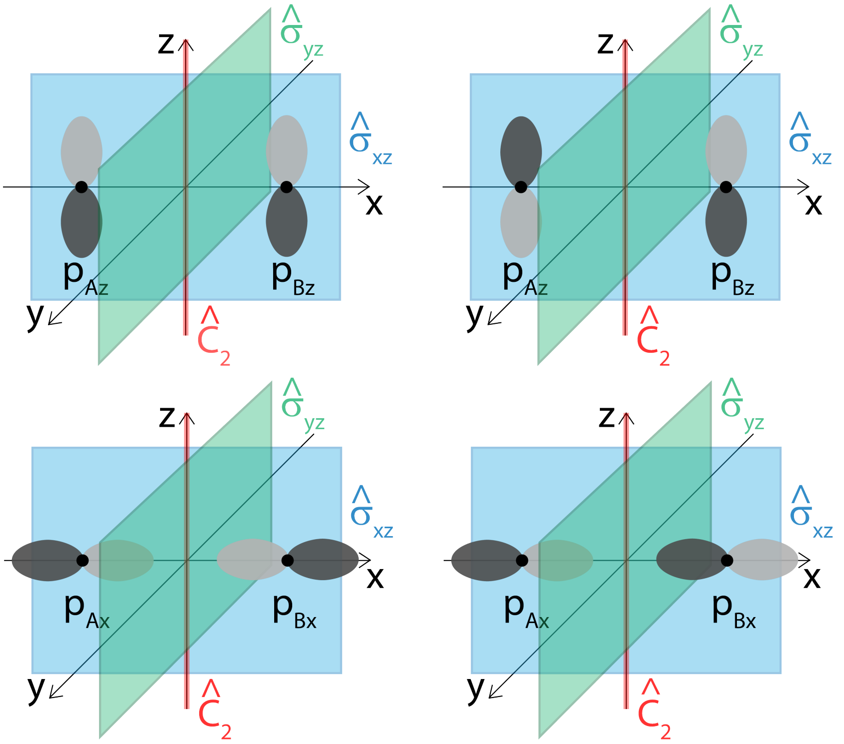

Figure 47: Adding of the p_z and p_x AOs on the atoms A and B. The two p AOs can be in-phase (left) or out-of-phase (right).

Equation 15 is only valid for non-degenerate orbitals. The sign sgn must be taken into account for every single-electron wavefunction.

$$\hat{O}\Psi = \prod_{i=1}^{n} sgn\hat{O}\psi_i \tag{16}$$

The irreducible representation $IRREP$ is definded by Equation 17.

$$IRREP(\Psi) = \prod_{i=1}^{n} IRREP(\psi_i) \tag{17}$$

Figure 17 represents the LC of the AOs on the atoms A and B that lead to the bonding and anti-bonding σ and π MOs. Table 48 can be constructed by performing the symmetry operators of the point group C_{2v} on the constructed MOs.

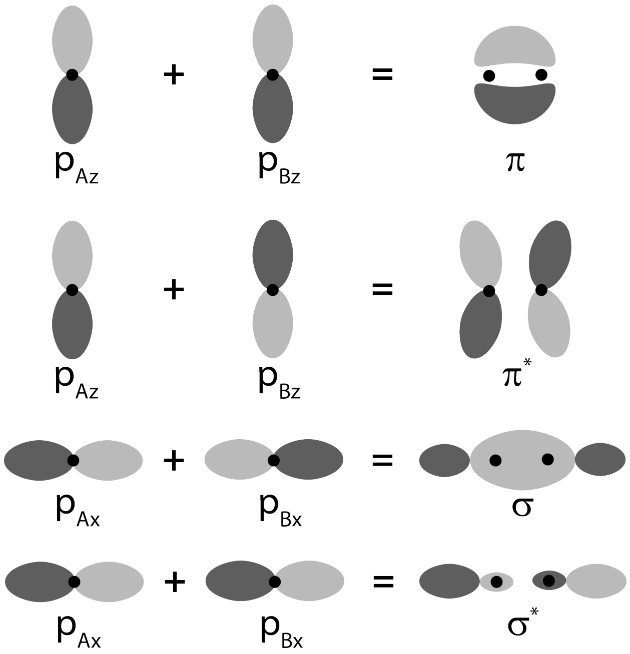

Figure 48: Formation of the delocalized MOs that describe a double bond via LCAO.

Table 7: Summary of the transformation behaviour of the delocalized MOs under the symmetry operations of the point group C_{2v}.

$\hat{\mathbf{E}}$	$\hat{\mathbf{C}}_\mathbf{2}$	$\hat{\sigma}_{\mathbf{xz}}$	$\hat{\sigma}_{\mathbf{yz}}$
σ	σ	σ	σ
σ^*	$-\sigma^*$	σ^*	$-\sigma^*$
π	π	π	π
π^*	$-\pi^*$	π^*	$-\pi^*$

A.3 Woodward-Hoffmann Rules

In the description of chemical reactivity using MO theory, the frontier orbitals HOMO and LUMO of the reactants and products are most important. At the beginning of the chemical reaction, all HOMOs of the reactants are doubly occupied, all LUMOs are unoccupied. During the reaction electrons from the HOMOs are transferred to the LUMOs. This picture of a chemical reaction is called the acceptor-donor picture. See [25], chapters 14.6 and 14.7. The donating of electrons can also be expressed by saying that the HOMO of one reactant and a LUMO of another reactant are linearly combined giving a bonding and an antibonding MO of the product and that the bonding product MO is occupied by the electrons residing before in the HOMO. If during the whole reaction some symmetry elements of the nuclear framework are conserved, the symmetry elements define the symmetry group of the reaction and both the frontier orbitals of the reactants and the frontier orbitals of the product must transform according to IRREPs of the symmetry group and only orbitals belonging to the same IRREP can be linearly combined. Next, the occupancy of the sets of LCs of the reactant frontier orbitals and of the set of product frontier orbitals is compared. Whenever a large barrier is found for the reaction there is a correlation of the occupied LCs with the occupied product orbitals belonging to the same IRREP, the reaction is symmetry forbidden. If however occupied LCs correlate with occupied product orbitals and unoccupied LCs correlate with unoccupied product orbitals, the reaction is symmetry allowed. However, there are reactions with very small barriers although occupied reactant MOs correlate with unoccupied product MOs and vice versa and symmetry allowed reactions may have a barrier. So, orbital correlation is not able to predict large or small barriers, but large barriers can be explained with orbital correlation.

For the dimerization of $H_2X + XH_2$ Figure A.3 shows the symmetry elements that are used to label MOs and LCs of reactant MOs.[13]. All orbitals can be uniquely labelled using two symmetry elements, e.g. the two two-fold

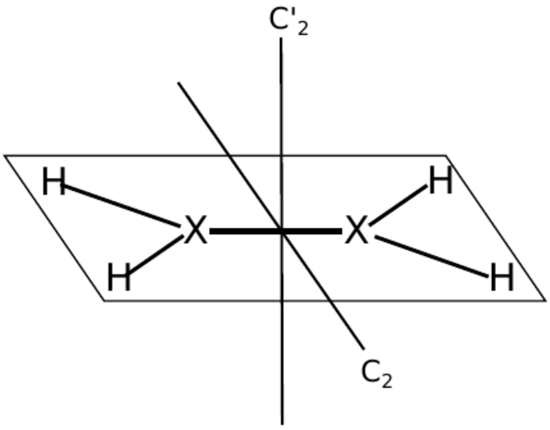

Figure 49: The symmetry elements for the dimerization of XH_2 in D_{2h} symmetry.

rotation axes shown in Figure A.3. During cis-bending the symmetry element C_2 is destroyed and the symmetry element C'_2 survives, while during trans-bending the symmetry element C'_2 is destroyed and the symmetry element C_2 survives. The reactant frontier orbitals are the two σ-type hybrid AOs h and the two p AOs. In the SiH_2 fragment the LP electrons occupy the hybrid AO h. In the ground state of CH_2 the LP electrons occupy the AOs h and p. The frontier orbitals of the product are the σ, σ^*, π and π^* MOs. The mapping of the four reactant AOs used in the dimerization of

Table 8: Mapping of the four reactant AOs used in the dimerization of XH_2 fragments.

Symmetry Operation	$\mathbf{h_A}$	$\mathbf{h_B}$	$\mathbf{p_A}$	$\mathbf{p_B}$
$\hat{\mathbf{C}}'_\mathbf{2}$	h_B	h_A	p_B	p_A
$\hat{\mathbf{C}}_\mathbf{2}$	h_B	h_A	$-p_B$	$-p_A$

XH_2 under the symmetry operations is given in Table 8. The two fragments are labelled A and B. Using $p+p$ instead of p_A+p_B etc. for the LCAOs, the classification of the LCAOs and of the product MOs is as given in Table 9.

Table 9: Symmetry labels of the orbitals involved in the XH_2 dimerization reaction. The labels are with respect to the two two-fold rotation axes shown in Figure A.3. When the symmetry of the system is reduced, the symmetry classification is done with respect to the surviving symmetry element.

Fragments			**Product**		
LC of FOs	$\hat{\mathbf{C}}'_2$	$\hat{\mathbf{C}}_2$	**MO**	$\hat{\mathbf{C}}'_2$	$\hat{\mathbf{C}}_2$
$p-p$	A	S	π^*	A	S
$p+p$	S	A	π	S	A
$h-h$	A	A	σ^*	A	A
$h+h$	S	S	σ	S	S