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Multireference Hilbert Space Coupled Cluster Methods

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Abstract

In this Thesis I have summarized our research on the Hilbert space multireference coupled cluster methods. Single-reference coupled cluster methods represent now well established and routinely applicable techniques in the computational chemistry and yield highly accurate results for most molecules close to their equilibrium geometry. However, when studying chemical processes, one inevitably encounters systems which have a multiconfigurational nature, for example some transition states, conical intersections, diradicals, etc., and are thus poorly described by single-reference methods (at practical truncation levels).

In contrast to the single-reference coupled cluster method, the development of its multireference counterpart is still a topic of active research, since such an extension is neither straightforward nor unique and several possible pathways have been proposed. The Hilbert-space multireference coupled cluster methods, which this Thesis is concerned with, represent the pathway which we have followed and where we have contributed. The Thesis is based on 27 publications in peer-reviewed international journals spanning more than a decade of research on the MRCC field, which I started after joining the J. Heyrovský Institute of Physical Chemistry.

First, to open the Thesis, a brief survey of the coupled cluster method and overview of different approaches to its multireference generalization is given in the *Introduction*.

The second chapter entitled *Overview of Hilbert-space multireference CC methods* starts with a few sections reviewing the basis of the MRCC theory — CC ansatz, multireference perturbation theory, Jeziorski-Monkhorst ansatz, and the effective Hamiltonian. Then the four variants of the Hilbert-space multireference CC methods are described in the chronological order of their invention: first the state-universal method, then the Brillouin-Wigner method (BWCC), which was the first state-specific MRCC method proposed. Since BWCC theory is not size-extensive, it was necessary to devise size-extensivity corrections, which are also described in this section. Then follows the Mukherjee’s MRCC method (MkCC) and its equivalent linked formulation which we introduced, and finally, for the sake of completeness, also a section describing the H2E2 method proposed by Mahapatra and Chattopadhyay.

The third chapter *Triexcitations in the Hilbert-space MRCC* summarizes our development of MRCC methods with triexcitations. In its first section the full iterative triexcitations for BWCC and MkCC methods are presented, while the second section is devoted to perturbative triexcitations approaches, which are computationally less demanding. The state-universal method with triexcitations developed by Bartlett et al. is first reviewed, then our BWCCSD(T) and MkCCSD(T_n) methods are introduced. The MkCCSD(T_i) variant introduced by Evangelista et al. is compared with our approaches, and finally, our MkCCSD(T_u) version of the method is described, which avoids the intruder state problem without the necessity to iterate the T_3 amplitudes

The fourth chapter *Illustrative numerical results* presents a few computational results showing properties and performance of the developed methods. These include a study of the effect of triexcitations on the spectroscopic constants of the oxygen molecule, assessment of various versions of the Mukherjee’s MRCC method with triexcitations on the BeH_2 model investigating the effect of intruder states, and a study of the singlet-triplet gap in the tetramethyleneethane molecule by Brillouin-Wigner and Mukherjee’s MRCC methods with triexcitations. The selection is only illustrative, an extensive collection of numerical results is present in the papers attached to the Thesis.

The Thesis closes with *Conclusions*, summarizing the general results of our research and indicating possible future directions.

Contents

1	Introduction	4
2	Overview of Hilbert-space multireference CC methods	5
2.1	Multireference perturbation theory	5
2.2	Jeziorski-Monkhorst ansatz	6
2.3	Effective Hamiltonian in MRCC theories	7
2.4	State-universal MRCC method	7
2.5	Brillouin-Wigner MRCC method	8
2.6	BWCC size-extensivity corrections	8
2.7	Mukherjee’s MRCC method	9
3	Triexcitations in the Hilbert-space MRCC	9
3.1	Full iterative inclusion of triexcitations	10
3.1.1	BWCCSDT	10
3.1.2	MkCCSDT	10
3.1.3	Uncoupled approximation to MkCCSDT	11
3.2	Perturbative triexcitations	11
3.2.1	SU CCSD(T)	11
3.2.2	BWCCSD(T)	12
3.2.3	MkCCSD(T_n)	12
3.2.4	MkCCSD(T_i)	13
3.2.5	MR MkCCSD(T_u)	13
4	Illustrative numerical results	14
4.1	Oxygen	14
4.2	BeH ₂	14
4.3	Singlet-Triplet Separation in the Tetramethyleneethane	15
5	Conclusions and outlook	18

1 Introduction

Quantum chemical calculations have become in the last decades an indispensable part of both basic and applied research in chemistry. Despite the huge progress in the density functional methods, which are today most popular among computational chemists due to their relatively low computational cost, there is still a need for more accurate wave function methods. Such methods are able to describe electron correlation effects with a systematically improvable accuracy and high reliability.¹ A prominent representative of this class of methods is the coupled cluster theory (CC), introduced to quantum chemistry by *ék*.² The single-reference coupled cluster method with mono- and biexcitations and perturbative inclusion of triexcitations (CCSD(T)) is today considered a “golden standard” of computational chemistry, and it is available in many program packages and employed widely in a big variety of chemical applications.³

Despite this success and enormous progress since the pioneering years, the coupled cluster theory remains an active research field.³⁻⁷ Particularly its generalizations to systems with several reference configurations, needed for description of molecules with open shell or (quasi)degeneracies, are still not as simply and straightforwardly applicable as standard single-reference methods. Solving this problem represents an interesting as well as important goal, since there are several classes of chemically interesting systems, which are due to the quasidegeneracies not easily accessible to single-reference methods. It is natural to expect that multireference CC methods should play such a prominent role in description of these systems, as the standard CC plays among single-reference methods.

During past years, many approaches how to apply the coupled cluster method to multireference problems have been suggested, which can be roughly categorized to the following (not at all exhaustive) list: (i) Methods based on a single-reference expansion, which employ formally a single Fermi vacuum and include higher excitations with indices partially limited to an active space.⁸⁻¹² (ii) Externally and internally corrected and reduced multireference CCSD methods,¹³⁻¹⁷ which extract information about the most important higher excitations or active space mono and biexcitations from an external calculation by a different method like CASSCF or MRCl.¹³⁻¹⁷ (iii) Method of moments CC and (completely) renormalized CC methods, which are based on a CC energy correction computed from projections of the CC wave function to higher excited determinants.¹⁸⁻²² (iv) Fock space multireference CC methods,²³⁻²⁶ similarity-transformed methods²⁷⁻³⁰ and spin-flip methods,³¹⁻³³ whose common feature is the use of a single Fermi vacuum, from which the states under study are generated by addition or subtraction of electrons or by a spin flip of some electrons. (v) Hilbert space multireference CC methods³⁴⁻³⁹ based on the wave operator in the Jeziorski-Monkhorst form³⁴ or modifications thereof, where each reference configuration represents one Fermi vacuum and has its set of amplitudes.

The Hilbert-space multireference coupled cluster methods, which this Thesis is concerned with, represent the pathway which we have followed and where we have contributed. The state-specific Brillouin-Wigner MRCC method originally proposed by Hubač, Mášik, and Čársky,^{37,40,41} is a computationally tractable method resistant with respect to intruder states. Our first result was an efficient implementation of this method with mono and biexcitations (BWCCSD),³⁸ later extended to a larger number of reference configurations also with open shells.^{42,43} It has turned out, that this method lacks size-extensivity, which can cause a big error when computing energy differences (like e.g. reaction energies or dissociation energies).⁴⁴ We have therefore developed a size-extensivity correction to the BWCC method in an a posteriori form^{45,46} and later in the iterative form.⁴⁷ The BWCC methods has been successfully applied to a whole range of molecules from diatomics^{42-44,48-50} to organic diradicals.⁵¹⁻⁵⁶ The state-specific Mukherjee MRCC method

was proposed later than the BWCC method^{36,57} and its main advantage is the exact size-extensivity. Several groups including us have been involved in its development during the past decade. Presently it seems more promising than the BWCC method, however, it still lacks some important features, mainly the invariance with respect to active orbital rotations.

An extensive numerical experience with single-reference coupled cluster methods has shown, that the truncation of the cluster operator at the singles and doubles level does not yield results of chemical accuracy (e.g. for reaction or activation energies). To achieve this level of accuracy, it is necessary to include also triexcitations, either exactly at the CCSDT level,^{58,59} or in a perturbative way CCSD(T).⁶⁰ When also static correlation plays a role, triexcitations should similarly be included to the MRCC methods. We have included triexcitations to the BWCC method in both iterative^{61,62} and non-iterative⁶³ manner, as well as to the MkCC method.^{64,65}

This thesis attempts to provide a concise overview of the Hilbert-space MRCC theory with emphasis on our own contributions to the field. The topics covered in individual chapters of the Thesis are summarized below.

2 Overview of Hilbert-space multireference CC methods

This section of the Thesis gives an overview of the Hilbert-space multireference CC methods. It starts with introductory paragraphs about the CC exponential ansatz and multireference perturbation theory, introduces the Jeziorski-Monkhorst Ansatz and Effective Hamiltonian. Finally, our contributions to the BWCC and MkCC methods in general and at the singles and doubles level are also covered in this section.

2.1 Multireference perturbation theory

The multireference perturbation theory is conveniently formulated by means of the wave operator and Bloch equation.^{67,68} As usually in the perturbation theory, one splits the total Hamiltonian to an unperturbed one and perturbation

$$H = H_0 + V \quad (1)$$

The eigenfunctions of the unperturbed Hamiltonian H_0 are assumed to be known and will be denoted as Φ_μ . Then one defines an M -dimensional model space \mathcal{P} spanned by Φ_μ , $\mu = 1, \dots, M$, and its orthogonal complement \mathcal{Q} . The appropriate projection operators are denoted P and $Q = 1 - P$. The α -th eigenfunction of the full Hamiltonian H is assumed to have a nonzero projection onto the model space

$$\Psi_\alpha^P \equiv P\Psi_\alpha = \sum_{\mu=1}^M c_\mu^\alpha \Phi_\mu \quad (2)$$

The wave operator Ω_α transforms such a projection back to the eigenfunction of the exact Hamiltonian

$$\Psi_\alpha = \Omega_\alpha \Psi_\alpha^P \quad (3)$$

and it may in general be state-specific, carrying thus the subscript α . The intermediate normalization

$$\langle \Psi_\alpha | \Psi_\alpha^P \rangle = 1 \quad (4)$$

can be used, if the model space \mathcal{P} is complete, i.e. contains all Slater determinants possible for a selected subset of active orbitals, given z -projection of the spin, and spatial symmetry. In such a case, the wave operator must not generate excitations which would transform the reference functions Φ_μ , $\mu = 1, \dots, M$ between each other and it holds

$$P\Omega_\alpha P = P \quad (5)$$

The exact energy is then obtained as the eigenvalue of a (non-Hermitian) effective Hamiltonian, which has the form

$$H_\alpha^{\text{eff}} = PH\Omega_\alpha P \quad (6)$$

In the state-specific (SS) theories, only its α -th eigenvalue

$$H_\alpha^{\text{eff}}\Psi_\alpha^P = E_\alpha\Psi_\alpha^P \quad (7)$$

has a physical meaning, while in the state-universal (SU) theory its whole spectrum corresponds to a subset of the spectrum of H . We will omit the subscript α at the effective Hamiltonian henceforth, since the type of the formalism (SU or SS) is always clear from the context.

In order to obtain the exact wave function from the model space projection, one has to determine the wave operator, i.e. to construct the Bloch equation, which it has to obey. In the framework of RSPT, the Bloch equation reads^{67,68}

$$[\Omega, H_0]P = V\Omega P - \Omega PV\Omega P \quad (8)$$

which can be cast to the equivalent form

$$H\Omega P = \Omega PH\Omega P \equiv \Omega H^{\text{eff}} \quad (9)$$

The wave operator obtained by solving this Bloch equation is state-universal. On the other hand, Hubač et al.^{37,40,41} derived a state-specific BW form of the Bloch equation

$$\Omega_\alpha = 1 + B_\alpha V\Omega_\alpha \quad (10)$$

where B_α is the BW resolvent

$$B_\alpha = \frac{Q}{E_\alpha - H_0} \quad (11)$$

The state-specific MRCC methods can be derived from this Bloch equation or directly from the Schrödinger equation.

2.2 Jeziorski-Monkhorst ansatz

The basis of the Hilbert-space multireference CC methods is the Jeziorski-Monkhorst ansatz³⁴ for the wave operator

$$\Omega_\alpha = \sum_{\mu=1}^M e^{T_\alpha(\mu)} |\Phi_\mu\rangle \langle \Phi_\mu| \quad (12)$$

In principle, without any truncation of the $T(\mu)$ operators, one can still recover the exact energy with this ansatz, however, in practice the cluster operators $T(\mu)$ are truncated in the same way as in the single reference CCSD, CCSDT, ... approximations. Note also that the reference determinant Φ_μ plays the role of a Fermi vacuum for the excitation operators in $T(\mu)$, each set of amplitudes has thus its own Fermi vacuum. For the

aforementioned complete model space, to achieve the intermediate normalization (4), the amplitudes in $T(\mu)$ which transform Φ_μ to another $\Phi_\nu \in \mathcal{P}$ are set to zero.

Notice that within the JM Ansatz a given determinant from the orthogonal complement of the model space can in general be obtained from several reference determinants via different excitations. This inherent redundancy can, however, be resolved uniquely in the state universal methods (see below), which provide enough equations to uniquely determine all the amplitudes in the JM Ansatz. In the state-specific methods, one solves this problem by imposing certain additional ‘‘sufficiency conditions’’ which lead to a unique particular solution of the otherwise underdetermined system of equations. The choice of the sufficiency conditions is not unique, however, giving rise to different SS methods like BWCC or MkCC. In the latter case the sufficiency conditions have been chosen in such a way to guarantee exact size-extensivity of the method.^{36,57,78}

2.3 Effective Hamiltonian in MRCC theories

The effective Hamiltonian eigenvalue equation (7) follows from the Schrödinger equation for state α

$$H\Psi_\alpha = E_\alpha\Psi_\alpha \quad (13)$$

to which the wave operator definition (3) is inserted. Using the intermediate normalization condition and expanding $P\Psi_\alpha$ in the model space determinants leads to the matrix form of the H^{eff} eigenvalue equation

$$\sum_{\nu}^M H_{\mu\nu}^{\text{eff}} c_{\nu}^{\alpha} = E_{\alpha} c_{\mu}^{\alpha} \quad (14)$$

where for the methods based on the Jeziorski-Monkhorst ansatz and employing a complete model space the effective Hamiltonian matrix elements are

$$H_{\nu\mu}^{\text{eff}} = H_{\mu\mu}\delta_{\nu\mu} + \langle\Phi_{\nu}|H_N(\mu)e^{T(\mu)}|\Phi_{\mu}\rangle_C \quad (15)$$

Notice the similarity of the diagonal H^{eff} matrix elements with the energy expression in the single-reference CC — the only difference being that it is taken with respect to the Fermi vacuum of the particular reference configuration.

2.4 State-universal MRCC method

The state-universal MRCC method was historically the first representative of the Hilbert-space MRCC family.³⁴ The amplitude equations are derived by insertion of the Jeziorski-Monkhorst Ansatz into the Bloch equation. Two different formulations are possible, which are however equivalent as long as complete model space is employed. The amplitude equations in the Jeziorski-Monkhorst (connected) formulation are

$$\langle\Phi_{\vartheta}|H_N(\mu)e^{T(\mu)}|\Phi_{\mu}\rangle_C \equiv \langle\Phi_{\vartheta}|e^{-T(\mu)}H_N(\mu)e^{T(\mu)}|\Phi_{\mu}\rangle = \sum_{\nu\neq\mu} \langle\Phi_{\vartheta}|e^{-T(\mu)}e^{T(\nu)}|\Phi_{\nu}\rangle H_{\nu\mu}^{\text{eff}} \quad (16)$$

while in the Kucharski-Bartlett (linked) formulation they become

$$\langle\Phi_{\vartheta}|H_N(\mu)e^{T(\mu)}|\Phi_{\mu}\rangle_{C+DC,L} = \sum_{\nu\neq\mu} \langle\Phi_{\vartheta}|e^{T(\nu)}|\Phi_{\nu}\rangle H_{\nu\mu}^{\text{eff}} \quad (17)$$

The worst problem of the state-universal method (equally present in both versions) is, however, the poor convergence behavior due to the intruder state problem. The state-specific methods described in the following sections represent a possible cure of this problem.

2.5 Brillouin-Wigner MRCC method

The Brillouin-Wigner CC method, proposed by Hubač et al.,^{37,40,41,85–87} was historically the first state-specific Hilbert-space MRCC approach. A review of Brillouin-Wigner methods in many-body theory has recently been published by Hubač and Wilson;⁸⁸ we have coauthored also several monography chapters dedicated to MRCC theory.^{89–92}

Our research in the MRCC field started with an efficient implementation and numerical assessment of the BWCC method in the Aces II program.³⁸ We have then introduced the size-extensivity corrections for BWCC and performed their assessment^{44,46,47} and later developed also analytic gradient for the BWCCSD method.⁹³ The corrected BWCC has been successfully applied to several systems, ranging from model systems and biatomics to mid-sized molecules: BeH₂ model,⁹⁴ potential curves of IBr,⁴² O₂,⁴³ CaC and ZnC,⁴⁸ and NF⁵⁰ molecules, singlet-triplet gap in tetramethyleneethane⁵² and in alkylcarbenes,⁵⁴ automerization barrier of cyclobutadiene,⁵¹ activation and reaction energy of the Bergmann cyclization,⁵³ ring-opening of methylenecyclopropane and singlet-triplet gap in trimethylenmethane.⁵⁶

The original derivation of the BWCC method^{37,87} was based on the BW Bloch equation (10) with the BW resolvent (11). However, a more straightforward derivation is possible, where one starts directly from the Schrödinger equation and inserts the Jeziorski-Monkhorst ansatz (12) for the Ω operator in it. The resulting amplitude equation reads

$$\sum_{\mu} [He^{T(\mu)} - E_{\alpha}e^{T(\mu)}] |\Phi_{\mu}\rangle c_{\mu}^{\alpha} = 0 \quad (18)$$

In the state-specific context this equation system is underdetermined, since the number of variables in all $T(\mu)$ generally exceeds the number of available projections $\cup_{\mu} \langle \Phi_{\vartheta}(\mu) |$. One has to apply the sufficiency conditions, requiring that individual terms in the summation in (18) vanish, yielding after a projection to bras excited from every reference individually

$$\langle \Phi_{\vartheta}(\mu) | [He^{T(\mu)} - E_{\alpha}e^{T(\mu)}] |\Phi_{\mu}\rangle = 0 \quad (19)$$

To obtain computationally practicable amplitude equations, the Hamiltonian can be expressed in the normal ordered form and the resulting terms are split to connected, disconnected but linked, and unlinked diagram contributions, yielding finally

$$(E_{\alpha} - H_{\mu\mu}^{\text{eff}}) \langle \Phi_{\vartheta} | e^{T(\mu)} | \Phi_{\mu} \rangle = \langle \Phi_{\vartheta} | H_N(\mu) e^{T(\mu)} | \Phi_{\mu} \rangle_{C+DC,L} \quad (20)$$

2.6 BWCC size-extensivity corrections

In our first study on the BWCC topic³⁸ we have investigated the CH₂ and SiH₂ diradicals as well as the twisted ethylene. The relatively larger errors found for the latter already indicated that the size-inextensivity of BWCC cannot be neglected. This has motivated us to develop an a posteriori size-extensivity correction,⁴⁶ based on an observation that the Brillouin-Wigner denominator coming from the resolvent (11) can be expressed in terms of the Rayleigh-Schrödinger denominator plus a size-inextensive term

$$\frac{1}{D_{\vartheta}(\mu) + E_{\alpha} - H_{\mu\mu}^{\text{eff}}} = \frac{1}{D_{\vartheta}(\mu)} - \frac{E_{\alpha} - H_{\mu\mu}^{\text{eff}}}{D_{\vartheta}(\mu)[D_{\vartheta}(\mu) + E_{\alpha} - H_{\mu\mu}^{\text{eff}}]} \quad (21)$$

In practical calculations the correction has been applied by dropping size-inextensive terms originating from the second r.h.s. term in an additional iteration of cluster amplitudes after BWCC convergence has been achieved.

Another path towards the size-extensivity correction for BWCC, which we followed in Ref.,⁴⁷ is based on a generalized Bloch equation, which contains (9) and (10) as its special cases. In this formalism the a posteriori size-extensivity correction corresponds to iterating amplitude equations

$$\begin{aligned} \lambda(E_\alpha - H_{\mu\mu}^{\text{eff}})\langle\Phi_\vartheta|e^{T(\mu)}|\Phi_\mu\rangle &= \langle\Phi_\vartheta|H_N(\mu)e^{T(\mu)}|\Phi_\mu\rangle_{C+DC,L} \\ &- (1-\lambda)\sum_{\nu\neq\mu}\langle\Phi_\vartheta|e^{T(\nu)}|\Phi_\nu\rangle H_{\nu\mu}^{\text{eff}} \end{aligned} \quad (22)$$

with $\lambda = 1$ until convergence and then performing an additional iteration setting $\lambda = 0$ to get corrected amplitudes, which are in turn used to build the corrected effective Hamiltonian, which is then diagonalized to get the corrected energy.

2.7 Mukherjee’s MRCC method

The starting point for the derivation of the Mukherjee’s MRCC method (MkCC) is – similarly to the BWCC method – the Schrödinger equation with the Jeziorski-Monkhorst ansatz inserted (18). However, rather than immediately splitting the sum over μ , Mukherjee et. al.³⁶ proposed to use a resolution of identity in the form

$$\begin{aligned} 1 &= e^{T(\mu)}e^{-T(\mu)} = e^{T(\mu)}(P+Q)e^{-T(\mu)} \\ &= \sum_{\nu=1}^M e^{T(\mu)}|\nu\rangle\langle\nu|e^{-T(\mu)} + e^{T(\mu)}Qe^{-T(\mu)} \end{aligned} \quad (23)$$

before the sufficiency conditions are applied. An essential step of the Mukherjee’s derivation is the interchange of the μ and ν summation indices, leading finally to the amplitude equations

$$\langle(\Phi_\mu)_{i\dots}^{a\dots}|e^{-T(\mu)}He^{T(\mu)}|\Phi_\mu\rangle c_\mu^\alpha + \sum_{\nu\neq\mu} H_{\mu\nu}^{\text{eff}}c_\nu^\alpha \langle(\Phi_\mu)_{i\dots}^{a\dots}|e^{-T(\mu)}e^{T(\nu)}|\Phi_\mu\rangle = 0 \quad (24)$$

In contrast to both state universal and Brillouin-Wigner coupled cluster methods, the amplitude equations (24) explicitly contain the eigenvector coefficients c_μ^α and are also coupled through the effective Hamiltonian, as well as the matrix elements $\langle(\Phi_\mu)_{i\dots}^{a\dots}|e^{-T(\mu)}e^{T(\nu)}|\Phi_\mu\rangle$. Both the first and second term in Eq. (24) have been shown to be connected, which results in a rigorous size-extensivity of the approach.³⁶ Similarly to the SU MRCC method, a linked form of the amplitude equations can be derived

$$c_\mu^\alpha(E^\alpha - H_{\mu\mu}^{\text{eff}})\langle\Phi_\vartheta|e^{T(\mu)}|\Phi_\mu\rangle = \langle\Phi_\vartheta|H_N(\mu)e^{T(\mu)}|\Phi_\mu\rangle_{C+DC,L,EXT}c_\mu^\alpha + \sum_{\nu\neq\mu}\langle\Phi_\vartheta|e^{T(\nu)}|\Phi_\mu\rangle H_{\mu\nu}^{\text{eff}}c_\nu^\alpha \quad (25)$$

which is equivalent to (24) for complete model spaces. This form of the amplitude equations has a structure analogous to the BWCC equations (20) and explicitly shows the same Brillouin-Wigner shift of the denominators, but contains additional coupling terms and discards *DC*, *L* terms with all indices from the active orbital set.

3 Triexcitations in the Hilbert-space MRCC

As is well known from the single reference CC, triexcitations have to be included if one aims to achieve chemical accuracy. This section is devoted to the inclusion of triexcitations to MRCC methods, in an iterative manner (subsection 3.1) and perturbatively (subsection 3.2).

3.1 Full iterative inclusion of triexcitations

Our first contribution to this topic was the implementation of an approximation to the MR BWCCSDT method,⁶¹ followed by the implementation including all terms.⁶² Later we implemented and performed assessment of the MkCCSDT method in the linked formulation¹⁰⁰ and its uncoupled approximation.¹⁰¹ In the following subsections we will present the BWCCSDT and MkCCSDT methods.

3.1.1 BWCCSDT

The general amplitude equations (20) are valid for any truncation of the cluster operator. In the MR BWCCSDT method, we restrict the expansion to connected singles, doubles, and triples $T_{123}(\mu) = T_1(\mu) + T_2(\mu) + T_3(\mu)$. The T_3 operator gives rise to contributions to equations for T_1 and T_2 amplitudes, and additionally T_3 equations

$$\begin{aligned} [D_{ijk}^{abc}(\mu) + \lambda(E_\alpha - H_{\mu\mu}^{\text{eff}})]t_{ijk}^{abc}(\mu) &= \langle \Phi_{\mu_{ijk}}^{abc} | \hat{V}_N(\mu) e^{\hat{T}_{123}(\mu)} | \Phi_\mu \rangle_C + \\ &+ \lambda P(i/jk)P(a/bc) \{ (E_\alpha - H_{\mu\mu}^{\text{eff}})t_i^a(\mu) \tilde{\tau}_{jk}^{bc}(\mu) + \\ &+ \langle (\Phi_\mu)_i^a | \hat{H}_N(\mu) e^{\hat{T}_{123}(\mu)} | \Phi_\mu \rangle_C \tau_{jk}^{bc} + t_i^a \langle (\Phi_\mu)_{jk}^{bc} | \hat{H}_N(\mu) e^{\hat{T}_{123}(\mu)} | \Phi_\mu \rangle_C \}, \end{aligned} \quad (26)$$

where $D_{ijk}^{abc}(\mu)$ is the T_3 denominator

$$D_\nu(\mu) \equiv D_{ij\dots}^{ab\dots}(\mu) = F_{ii}(\mu) + F_{jj}(\mu) + \dots - F_{aa}(\mu) - F_{bb}(\mu) - \dots \quad (27)$$

The a posteriori size-extensivity correction is performed in the same manner as at the SD level, converging all amplitudes with $\lambda = 1$ and performing an additional iteration with $\lambda = 0$.

3.1.2 MkCCSDT

In section 2.7 we have presented two formulations of the MkCC method, which are equivalent when a complete model space is employed. The first MkCCSDT implementation, based on the connected formulation, was performed by Evangelista et al.¹⁰⁶ We have implemented the MkCC method with iterative triexcitations based on the linked formulation in the work.¹⁰⁰

For this purpose, the explicit form of the disconnected unlinked external terms in the amplitude equations (25) reads for T_2

$$\langle (\Phi_\mu)_{ij}^{ab} | H_N(\mu) e^{T(\mu)} | \Phi_\mu \rangle_{DC,L,EXT} = P(ij)P(ab) \langle (\Phi_\mu)_i^a | e^{-T(\mu)} H_N(\mu) e^{T(\mu)} | \Phi_\mu \rangle_C t_j^b(\mu) \quad (28)$$

and for T_3

$$\begin{aligned} \langle (\Phi_\mu)_{ijk}^{abc} | H_N(\mu) e^{T(\mu)} | \Phi_\mu \rangle_{DC,L,EXT} &= P(i/jk)P(a/bc) [\langle (\Phi_\mu)_{jk}^{bc} | e^{-T(\mu)} H_N(\mu) e^{T(\mu)} | \Phi_\mu \rangle_C t_i^a(\mu) \\ &+ \langle (\Phi_\mu)_i^a | e^{-T(\mu)} H_N(\mu) e^{T(\mu)} | \Phi_\mu \rangle_C \times \\ &\times (t_{jk}^{bc}(\mu) + t_j^b(\mu)t_k^c(\mu) - t_j^c(\mu)t_k^b(\mu))], \end{aligned}$$

where the terms with all bra indices from the active space are omitted. The connected term and the l.h.s. of (25) are identical to BWCC, while the last term of (25) reduces to products of the $T(\nu)$ amplitudes re-indexed with respect to the Fermi vacuum $|\Phi(\mu)\rangle$.

3.1.3 Uncoupled approximation to MkCCSDT

In the uncoupled version of the MkCC method proposed by Mukherjee et. al.,¹⁰⁷ the coupling term $\langle \Phi_\nu | e^{-T(\mu)} e^{T(\nu)} | \Phi_\mu \rangle$ is replaced by $\langle \Phi_\nu | e^{-T(\mu)} e^{T'_\nu(\mu)} | \Phi_\mu \rangle$, where $T'_\nu(\mu)$ corresponds to those components of $T(\mu)$ which give non-zero when acting on Φ_ν , i.e. excitations from orbitals occupied in both Φ_μ and Φ_ν into orbitals unoccupied in both Φ_μ and Φ_ν .

$$T'_\nu(\mu) = \sum_{i \dots \in \text{occ}(\mu) \cap \text{occ}(\nu)} \sum_{a \dots \in \text{virt}(\mu) \cap \text{virt}(\nu)} t'_\nu(\mu)_{i \dots}^{a \dots} a_a^\dagger \dots a_i \dots \quad (29)$$

In order to evaluate the couplings, we introduce the operator $\bar{T}(\mu)$ as the complement to $T'(\mu)$

$$\bar{T}_\nu(\mu) = T(\mu) - T'_\nu(\mu) \quad (30)$$

which obviously annihilates the Fermi vacuum Φ_ν

$$\bar{T}_\nu(\mu) | \Phi_\nu \rangle = 0. \quad (31)$$

In terms of the corresponding amplitudes, we may write

$$t_{i \dots}^{a \dots}(\mu) = t'_\nu(\mu)_{i \dots}^{a \dots} + \bar{t}_\nu(\mu)_{i \dots}^{a \dots}. \quad (32)$$

We have implemented this approximation at the SDT level; implementation details and numerical assessment of the uncoupled MkCCSDT method can be found in the paper.¹⁰¹ It has been shown that the effects of the uncoupled approximation are almost negligible when the small active space CAS(2,2) is employed, while they can grow (as expected from the nature of the approximation) for larger model spaces.

3.2 Perturbative triexcitations

Similarly to the single-reference case, the scaling of the methods with iterative triexcitations is prohibitive even for moderately sized molecules. To avoid this cost, perturbative approximations have been introduced and have achieved an enormous success at the single-reference level, CCSD(T) being often called a ‘‘golden standard’’ by computational chemists. We have thus worked on a perturbative inclusion of triexcitations in the multireference schemes, starting with the BWCCSD(T) method,⁶³ and later developing the MkCCSD(T_n)⁶⁴ and MkCCSD(T_u)⁶⁵ methods. Application of the BWCCSD(T) and MkCCSD(T) methods to a study of polycyclopentanes¹⁰⁸ and spiropentane¹⁰⁹ have also been published.

3.2.1 SU CCSD(T)

The first reported development of noniterative triples for Hilbert space MRCC methods was done by Balková and Bartlett¹¹⁰ in the state universal formulation. In their approach, after the SUCCSD equations are solved, the approximate triexcited amplitudes are obtained from the equation

$$t_{ijk}^{abc}(\mu) = \frac{\langle (\Phi_\mu)_{ijk}^{abc} | V_N(\mu) T_2(\mu) | \Phi_\mu \rangle_C - \sum_{\nu \neq \mu} [\langle (\Phi_\mu)_{ijk}^{abc} | T_2(\nu) | \Phi_\nu \rangle H_{\mu\nu}^{\text{eff}}]_C}{D_{ijk}^{abc}(\mu)}, \quad (33)$$

The perturbative correction is then performed on the matrix elements of the effective Hamiltonian (15). Since its diagonal elements are analogous to the single reference energy

diagrams, the diagonal corrections become a straightforward generalization of the single-reference CCSD(T), which reads

$$H_{\mu\mu}^{\text{eff}}(\text{T}) = H_{\mu\mu}^{\text{eff}}(\text{CCSD}) + E_T^{[4]}(\mu) + E_{ST}^{[5]}(\mu) + E_{ST}^{[4]}(\mu) \quad (34)$$

The off-diagonal elements of the effective Hamiltonian are calculated at the CCSDT-1 level using the linear contribution of T_3 to both T_1 and T_2 equations

$$H_{\nu\mu}^{\text{eff}}(\text{T}) = \langle \Phi_\nu | H_N(\mu) e^{T_{123}(\mu)} | \Phi_\mu \rangle_C^{\text{CCSDT-1}} = \langle \Phi_\nu | H_N(\mu) (e^{T_{12}(\mu)} + T_3(\mu)) | \Phi_\mu \rangle_C. \quad (35)$$

The CCSDT-1 level was chosen, since fourth order CCSD(T) terms can be viewed as the ones generated by the first iteration of CCSDT-1. Finally, the corrected energy is obtained by diagonalization of the triples-corrected effective Hamiltonian.

3.2.2 BWCCSD(T)

When developing the BWCCSD(T) method,⁶³ we have decided to follow an approach similar to the state-universal case, in particular to perform the corrections from connected triples also via the matrix elements of the effective Hamiltonian. The corrections to the diagonal H^{eff} elements consist formally of the same perturbative terms given by (34) as in the SU method. However, in contrast to the SU method, the triexcited amplitudes are obtained in a different way in the BWCC context

$$t_{ijk}^{abc}(\mu) = \frac{\langle (\Phi_\mu)_{ijk}^{abc} | V_N(\mu) T_2(\mu) | \Phi_\mu \rangle_C}{D_{ijk}^{abc}(\mu)}, \quad (36)$$

which reads explicitly in the integrals and amplitudes

$$t_{ijk}^{abc} = \frac{\sum_e P(i/jk) P(a/bc) t_{jk}^{ae} \langle bc || ei \rangle - \sum_m P(i/jk) P(a/bc) t_{mi}^{bc} \langle jk || ma \rangle}{D_{ijk}^{abc}} \quad (37)$$

Notice that we neglect the effect of nondiagonal Fock matrix elements in the T_3 equation, which would otherwise require an iterative solution of T_3 amplitudes.¹¹¹ Unfortunately it seems that the solution used in single reference theory, the semicanonical orbitals, cannot be generalized for MR cases, which leads to a non-invariance of the resulting method with respect to occupied-occupied and virtual-virtual rotations. This problem is shared by all the MR perturbative triples methods discussed here, however, the numerical effects have been found negligible in our study.⁶⁴ Numerical results of an assessment of the BWCCSD(T) method can be found in the paper,⁶³ where it was shown that for the three lowest lying states of the oxygen molecule the BWCCSD(T) method delivered results in a good agreement with iterative BWCCSDT ones.

3.2.3 MkCCSD(T_n)

The first attempt to include noniterative triexcitations in the MkCC method has been reported in our work.⁶⁴ We decided to neglect the coupling terms in (24) for the approximate T_3 amplitudes. As a justification we considered that in the single reference CCSD(T), only the term linear in T_2 is included at the right hand side of the T_3 equation, while the MkCC coupling terms in the T_3 equation contain either t_1 or t_3 cluster amplitudes as a factor. It is thus a plausible approximation in the MRCC T_3 equation to neglect them as well. After this approximation, only the terms in T_3 equations that contain a factor of C_μ^α are left and the eigenvector coefficient, if nonzero, can be eliminated from

the equation. The T_3 amplitude equation has thus the same form as the BWCCSD(T) one (36), differing only in that MkCCSD converged amplitudes are employed here. The drawback of this approximation is that the intruder state problem can emerge when D_{ijk}^{abc} in (36) approaches zero, as will be discussed in the next section.

As in the previous approaches, the diagonal H^{eff} elements are corrected according to eq. (34), the off-diagonal ones again at the CCSDT-1 level by eq. (35). The scheme is thus very similar to the MR BWCCSD(T) method, except for using converged MkCCSD T_1 and T_2 amplitudes as input for the (T) correction, of course.

3.2.4 MkCCSD(T_i)

Somewhat later a different approach has been presented by Evangelista et. al.,¹¹⁴ where corrections to the energy are explicitly evaluated, rather than corrections to $H_{\mu\nu}^{\text{eff}}$. Their derivation, which is based on a perturbative analysis of the MkCC Lagrangian,^{114–116} can be viewed as a multireference generalization of the Λ -CCSD(T)^{117–120} approach.

In MkCCSD(T_i), the amplitude equation for approximate T_3 includes the linear coupling terms

$$t_{ijk}^{abc}(\mu) = \frac{\langle (\Phi_\mu)_{ijk}^{abc} | V_N(\mu) T_2(\mu) | \Phi_\mu \rangle + \sum_{\nu \neq \mu} t_{ijk}^{abc}(\nu/\mu) H_{\mu\nu}^{\text{eff}} \frac{C_\nu^\alpha}{C_\mu^\alpha}}{D_{ijk}^{abc}(\mu) + (E^\alpha - H_{\mu\mu}^{\text{eff}})}. \quad (38)$$

Notice that MkCCSD(T_i) is resistant to intruders, due to the Brillouin-Wigner like denominator, but due to the presence of $t_{ijk}^{abc}(\nu/\mu)$ in the equation for $t_{ijk}^{abc}(\mu)$ the solution has to be performed iteratively, which is a considerable disadvantage.

3.2.5 MR MkCCSD(T_u)

The main motivation behind the development of the new approach which we presented in,⁶⁵ denoted MR MkCCSD(T_u), was to avoid the singularities in the MR MkCCSD(T_n) without the need for an iterative procedure to solve the triples equation as in MR MkCCSD(T_i). To achieve that, the uncoupled approximation described in section 3.1.3 can be employed to simplify the triples equation, which after moving linear T_3 terms to the left-hand side gives

$$t_{ijk}^{abc}(\mu) \left[D_{ijk}^{abc}(\mu) + \sum_{\nu \neq \mu}^\dagger H_{\mu\nu}^{\text{eff}} \frac{C_\nu^\alpha}{C_\mu^\alpha} \right] = \langle (\Phi_\mu)_{ijk}^{abc} | V_N(\mu) T_2(\mu) | \Phi_\mu \rangle_C - \sum_{\nu \neq \mu} \left[P(i/jk) P(a/bc) \bar{t}_{\nu i}^a(\mu) \bar{t}_{\nu jk}^{bc}(\mu) - P(ijk) \bar{t}_{\nu i}^a(\mu) \bar{t}_{\nu j}^b(\mu) \bar{t}_{\nu k}^c(\mu) \right] H_{\mu\nu}^{\text{eff}} \frac{C_\nu^\alpha}{C_\mu^\alpha} \quad (39)$$

where \dagger at the sum indicates that only terms where at least one of the i, j, k, a, b and c orbitals has a different occupation in the μ -th reference than in the ν -th one are included in the summation. Considering the triples equation (39), two advantages are observed. First notice that it yields $t_{ijk}^{abc}(\mu)$ in a single step rather than iteratively as in (38). Second, compared to the equation (36), this amplitude equation includes a denominator shift and is thus insensitive to intruder states. Numerical assessment of the approach presented in this section was performed on the BeH_2 model and on the tetramethyleneethane (TME) molecule.⁶⁵ It has been verified, that the singularities on the BeH_2 potential energy curve

present in MR MkCCSD(T_n) were removed by the new MR MkCCSD(T_u) method, which yields a smooth curve very close to the MR MkCCSD(T_i) or MR MkCCSDT-1 ones. The study of the TME molecule shows that to achieve even a qualitatively correct description of the singlet state, triexcitations have to be included in the MkCC method.

4 Illustrative numerical results

This section of the Thesis gives illustrative numerical examples of the performance of the state-specific Hilbert-space MRCC methods. The first example is the molecular oxygen, where a comparison with accurate spectroscopic data can be performed. While its ground state can be treated with single-reference methods, a correct description of the low-lying excited states requires a multireference treatment. The second example is the BeH₂ model system, which might seem somewhat artificial to a chemist, but it represents a stringent test of multireference methods. In particular, the performance of various versions of the MkCC method with non-iterative triples will be assessed on this example. The last example is the tetramethyleneethane molecule, which is a typical diradical with a close lying singlet and triplet state. Due to its multiconfigurational character, single-reference methods fail to describe its singlet state correctly and yield qualitatively incorrect values of the singlet-triplet energy gap, which can be cured by the multireference treatment. Many other numerical results can be found in the papers attached to the Thesis.

4.1 Oxygen

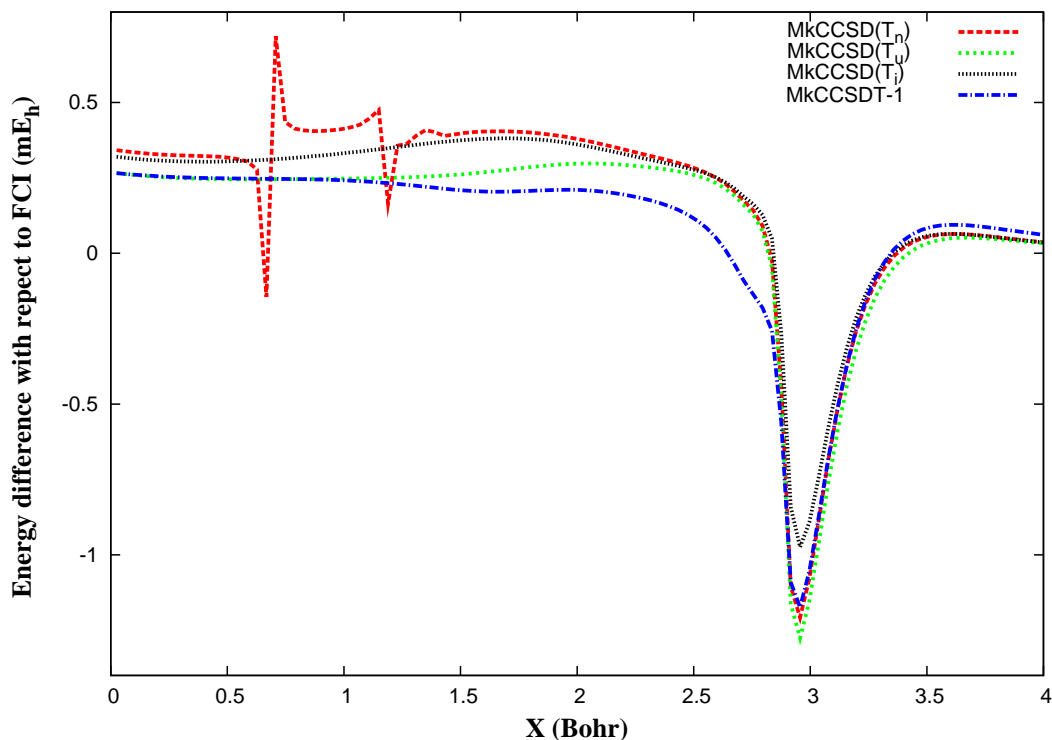
Three electronic states, the ground state $X^3\Sigma_g^-$ and the first two excited ones $a^1\Delta_g$ and $b^1\Sigma_g^+$ have been studied. The model space was spanned by four reference configurations formed within the active space of π_g anti-bonding orbitals occupied by two electrons. Due to spatial symmetry, the active space is complete.

The inclusion of triples lowers the vibrational frequency and elongates the bond length for both MR MkCC and MR BWCC methods. The change of the vibrational frequency can be almost 100 cm^{-1} , indicating the enormous importance of triexcitations. For oxygen molecule the spectroscopic constants obtained using triples are close to experimental data, confirming the importance of the triexcitations. The results obtained for bond lengths and vibrational frequencies show that the MR BWCC method is also able to yield spectroscopic constants correctly. However, the MR MkCC gives substantially better results for vertical excitation energies compared to MR BWCC, which can be attributed to its exact size-extensivity.

4.2 BeH₂

The BeH₂ model which describes the insertion of a beryllium atom to the H₂ molecule, confined to the C_{2v} symmetry, was introduced by Purvis et. al.¹²⁹ in 1983 to study single reference coupled cluster methods. Later it became popular in the study of various multireference methods.^{11,36,78,94,130-133} We employed the modified double ζ basis and CAS(2,2) orbitals as reported in,¹¹⁴ in order to make a comparison with this work possible. The deviations of total energy calculated by various MkCC approaches from FCI, are shown in Fig. 1. For all the approaches, the error curve has the same qualitative character: the deviations are relatively small in the single reference region, whereas in the multireference region the error grows to approximately $-1mE_h$. As reported in,¹¹⁴ the MkCCSD(T_n) method suffers from the intruder state problem for x in the range between

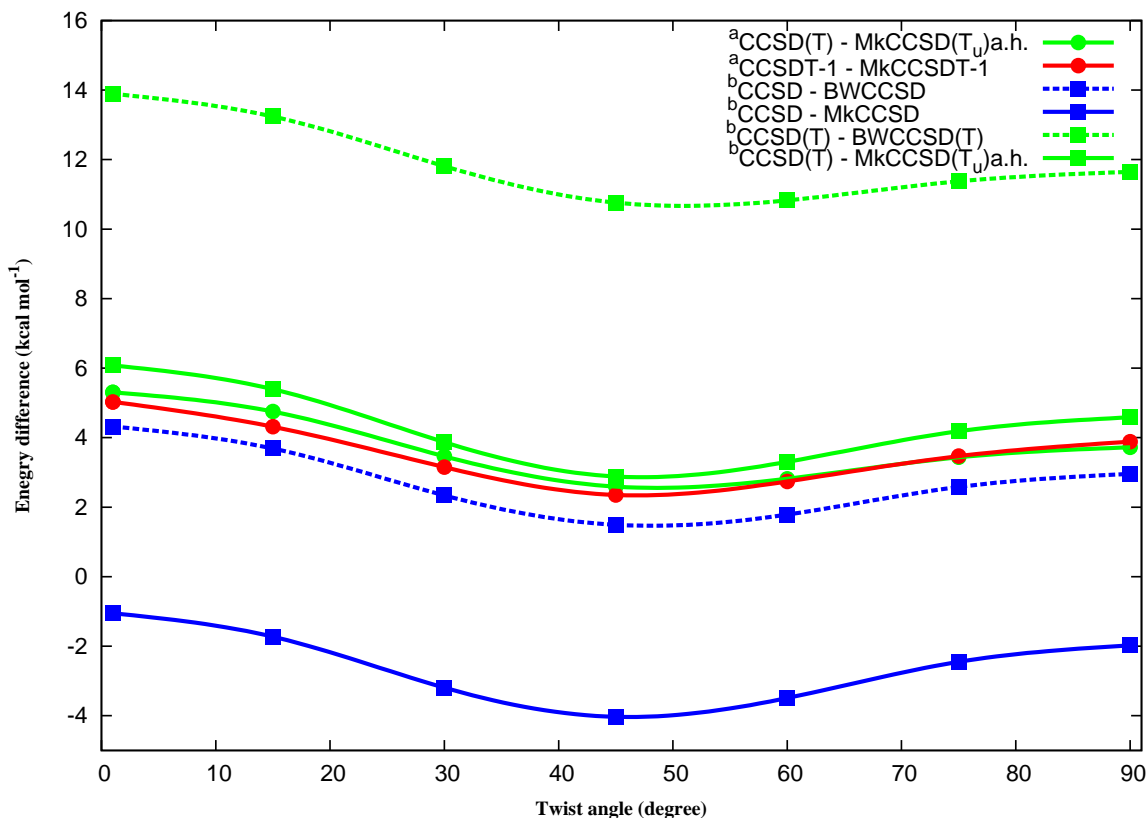
Figure 1: BeH₂: MkCC energy differences with respect to FCI



0.5 bohr and 1.5 bohr. Red, green, black and blue curves show errors of the MkCCSD(T_n), MkCCSD(T_u), MkCCSD(T_i), and MkCCSDT-1 methods, respectively, with respect to the FCI reference. The singularities exhibited by MkCCSD(T_n) near $x \approx 0.7, 1.2$ and 1.4 are removed in MkCCSD(T_u). The reason for this comes from the denominator shift in equation 39, which is identical to the BW shift for amplitudes with at least one active index. Furthermore, we can see that the MkCCSD(T_u) difference curve closely follows the MkCCSDT-1 one for x up to 2 bohr, in contrast to the MkCCSD(T_i). This difference can be explained by the absence of the nonlinear coupling terms (especially the T_1T_2 terms) in the MkCCSD(T_i) method.

4.3 Singlet-Triplet Separation in the Tetramethyleneethane

Tetramethyleneethane (TME) is a prototype of an unusual family of reactive intermediates called disjoint diradicals. In 1970, when P. Dowd reported preparation of TME and EPR its spectrum,¹³⁴ controversy started about its ground state, leading to many experimental and ab initio studies.^{52,135,135–143} Clifford et. al.¹⁴⁰ using the gas-phase negative ion photoelectron spectroscopy, revealed that the singlet state of TME is about 2 kcal mol⁻¹ below the triplet state, which was inconsistent with the previous matrix isolation EPR studies. They suggested that this discrepancy can be due to the fact that the matrix locks the TME at the triplet equilibrium structure at which singlet state is above the triplet state. Employing spin-restricted open-shell Kohn-Sham (ROKS) and spin-restricted ensemble-referenced Kohn-Sham (REKS), Filatov and Shaik¹⁴² found that TME has a minimum at D_{2d} geometry, where the triplet state is about 3 kcal mol⁻¹ above the singlet. Employing difference dedicated configuration interaction method (DDCI), Rodriguez et. al.¹⁴³ found that the singlet state is more stable than the triplet one for any

Figure 2: C₆H₈: Singlet-triplet gap

The singlet-triplet gap was obtained using ^a (cc-pVDZ) basis set and ^b (cc-pVTZ') is shown here.

conformation, but the energy difference decreases up to 0.29 kcal mol⁻¹ for the structure of the triplet minimum.

The singlet state of the TME diradical has a multireference character, while the triplet state is single reference in nature. The computed singlet-triplet gaps are shown in Figure 2. At all levels of theory, the ST curves have a very similar shape, with a single minimum near 45 degrees. However, the position of these curves varies significantly with the method used. The BWCCSD curve lies between 1 and 4 kcal mol⁻¹, which is in a good agreement with experiment and with previous study⁵² which employed MP2 geometries. However, the inclusion of perturbative triples increases the gap to 11 – 14 kcal mol⁻¹. Conversely, MkCCSD method performs rather poorly, predicting the wrong order of the two states. Inclusion of triples, both iterative and noniterative, increases the gap by approximately 7 kcal mol⁻¹, yielding values of ST gap between 2 and 6 kcal mol⁻¹. The MkCCSD(T_u) results lie very close to their MkCCSDT-1 counterparts. At the twisting angle 45°, the gap obtained was 2.6 kcal mol⁻¹ and 2.4 kcal mol⁻¹ for MkCCSD(T_u)/cc-pVDZ and MkCCSDT-1/cc-pVDZ, respectively. The relatively good performance of BWCCSD can be explained by a fortuitous compensation of errors caused on one hand by insufficient description of the dynamical correlation and on the other hand by the inaccuracy of the a posteriori size-extensivity correction. The difference between MkCCSD(T_u)/cc-pVDZ and MkCCSD(T_u)/cc-pVTZ' is less than 0.9 kcal mol⁻¹ at all twisting angles, confirming that the basis set effects are relatively minor.

The results obtained by MR MkCC with inclusion of triples are in agreement with the gas-phase negative ion photoelectron spectroscopy results by Clifford et. al.¹⁴⁰ This suggests

that the singlet state is more stable than the triplet one for any conformation with the energy gap minimum near 45° , although the limited size of the employed basis sets does not allow to claim this with certainty.

The study of the TME molecule shows that to achieve even a qualitatively correct description of the singlet state, triexcitations have to be included in the MkCC method. The good agreement of previous BWCCSD calculations on TME⁵² with experiment was thus caused by a fortuitous error cancellation between the inaccuracy of BWCC size-extensivity correction and the lack of dynamical correlation.

5 Conclusions and outlook

In this thesis we gave an overview of our work on the multireference coupled cluster field. We have been mainly involved in the development of Brillouin-Wigner MRCC method and of the Mukherjee’s MRCC method. We have developed several versions of these methods and implemented them in the ACES II program package, recently also in the CC-R12 and NWCHEM programs. We have performed performance assessment of the developed methods and several application calculations on systems exhibiting static correlation. Due to its exact size-extensivity, the Mukherjee’s method seems to be superior to the Brillouin-Wigner one, where it can be only be achieved approximately a posteriori size-extensivity correction. Unfortunately, MkCC method usually converges substantially slower than BWCC. MR MkCCSDT method gives the most accurate results from the methods investigated, however, the computational costs involved prevent its application to larger systems. Presently, the MR MkCCSD(T_u) method seems to be an adequate approach for accurate calculations of molecules exhibiting static correlation. It should perform similarly well as the CCSD(T) method does for systems dominated by a single Slater determinant, as long as the model space does not get too large. We have verified this behavior on several molecules with diradical character, where the active space consists of the HOMO-LUMO pair of orbitals. For such systems the MkCC method is already practically applicable and can be almost routinely employed. However, transition metal compounds or triple bond dissociation are not accessible yet since the accuracy of the MkCC method deteriorates for large model spaces, unless active tri- and tetraexcitations are taken into account. Moreover, its non-invariance to active orbital rotations represents another unpleasant feature, which hampers the widespread applicability. It can thus be predicted that the development of MRCC methods will remain subject of ongoing research by several groups worldwide.

We plan to continue our research on the multireference CC field in the near future, addressing several interesting topics. Presently we are working on the combination of the explicitly correlated (R12/F12) approach with the MRCC methods, which significantly speeds up the basis set convergence. Another direction of our effort is parallelization of the MRCC codes,¹⁴⁵ which should pave the way towards calculations of large molecules, efficiently employing modern supercomputers.

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Appendix A: Thesis publications

1. Pittner J., Nachtigall P., Čársky P., Mášik J., Hubač I.:
Assessment of the single-root multireference Brillouin–Wigner CCSD theory. Test calculations on CH₂, SiH₂, and twisted ethylene.
J. Chem. Phys., **110**, 10275–10282 (1999)
2. Hubač I., Pittner J., Čársky P.:
Size-extensivity correction for the state-specific multireference Brillouin–Wigner coupled-cluster theory
J. Chem. Phys., **112**, 8779–8784 (2000)
3. Sancho-García J. C., Pittner J., Čársky P., Hubač I.:
Multireference coupled-cluster calculations on the energy of activation in the automerization of cyclobutadiene: assessment of the state-specific multireference Brillouin–Wigner theory
J. Chem. Phys., **112**, 8785–8788 (2000)
4. Pittner J., Nachtigall P., Čársky P., Hubač I.:
State-specific Brillouin–Wigner multireference coupled cluster study of the singlet-triplet separation in the tetramethyleneethane diradical
J. Phys. Chem. A **105**, 1354–1356 (2001)
5. Pittner J., Šmydke J., Čársky P., Hubač I.:
State-specific Brillouin–Wigner multireference coupled cluster study of the F₂ molecule: Assessment of the a posteriori size-extensivity correction
J. Molec. Struc. (Theochem) **547**, 239–244 (2001)
6. Pittner J., Demel O., Čársky P., Hubač I.:
Four-reference state-specific Brillouin–Wigner coupled-cluster method: Study of the IBr molecule.
Int. J. Mol. Sci., **2**, 281–290 (2002)
7. Pittner J., Čársky P., Hubač I.:
Four- and 8-reference state-specific Brillouin–Wigner coupled-cluster method: Study of the singlet oxygen.
Int. J. Quant. Chem., **90**, 1031–1037 (2002)
8. Kerkines I., Pittner J., Čársky P., Mavridis A., Hubač I.:
On the ground states of CaC and ZnC: a multireference Brillouin–Wigner coupled cluster study
J. Chem. Phys. **117**, 9733–9739 (2002)
9. Pittner J.:
Continuous transition between Brillouin–Wigner and Rayleigh–Schrödinger perturbation theory, generalized Bloch equation, and application to the Hilbert space multireference coupled cluster method
J. Chem. Phys. **118**, 10876–10889 (2003).
10. Puiggros O. R., Pittner J., Čársky P., Stampfuss Ph., Wenzel W.:
Multireference Brillouin–Wigner coupled cluster singles and doubles (MR BWCCSD) and multireference doubles configuration interaction (MRDCI) calculations for the Bergman cyclization reaction Collect. Czech. Chem. Commun. **68**, 2309–2321 (2003).

11. Pittner J., Valdes-Gonzalez H., Gdanitz R. J., Čársky P.:
The performance of the multireference Brillouin-Wigner coupled cluster singles and doubles method on the insertion of Be into H₂
Chem. Phys. Lett. **386**, 211–215 (2004).
12. Demel O., Pittner J., Čársky P., Hubač I.:
Multireference Brillouin-Wigner coupled cluster singles and doubles study of the singlet-triplet separation in alkylcarbenes J. Phys. Chem. **A108**, 3125–3128 (2004).
13. Kardahakis S., Pittner J., Čársky P., Mavridis A.:
Multireference configuration interaction and coupled cluster calculations on the X³Σ⁻, a¹Δ, and b¹Σ⁺ states of the NF molecule
Int. J. Quant. Chem., **104**, 458–467 (2005)
14. Pittner J., Li X., Paldus J.:
Multireference Brillouin-Wigner coupled-cluster method with a general model space
Mol. Phys., **103**, 2239–2245 (2005).
15. Pittner J., Demel O.:
Towards the Multireference Brillouin-Wigner Coupled Clusters Method with Iterative Connected Triples: MRBWCCSDT-α Approximation
J. Chem. Phys., **122**, 181101 (2005).
16. Brabec J., Pittner J.:
The singlet-triplet gap in trimethylenmethane and the ring-opening of methylenecyclopropane: a multireference Brillouin-Wigner coupled cluster study
J. Phys. Chem. A **110**, 11765–11769 (2006)
17. Demel O., Pittner J.:
Multireference Brillouin-Wigner Coupled Clusters Method with Noniterative Perturbative Connected Triples
J. Chem. Phys., **124**, 144112 (2006).
18. Pittner J., Šmydke J.:
Analytic Gradient for the Multireference Brillouin-Wigner Coupled-Cluster Method and for the State-Universal Multireference Coupled-Cluster Method
J. Chem. Phys., **127**, 114103 (2007).
19. Demel O., Pittner J.:
Multireference Brillouin-Wigner Coupled Clusters Method with Singles, Doubles, and Triples: Efficient Implementation and Comparison with Approximate Approaches
J. Chem. Phys., **128**, 104108 (2008).
20. Bhaskaran-Nair K., Demel O., Pittner J.:
Multireference State-Specific Mukherjee's coupled cluster method with non-iterative triexcitations
J. Chem. Phys. **129**, 184105 (2008).
21. Veis L., Čársky P., Pittner J., Michl J.:
Coupled Cluster Study of Polycyclopentanes: Structure and Properties of C₅H_{2n}, n = 0 - 4
Coll. Czechosl. Chem. Commun. **73**, 1525 (2008).

22. Pittner J., Piecuch P.:
Method of Moments for the Continuous Transition Between Multireference Brillouin-Wigner and Rayleigh-Schrödinger Coupled Cluster Theories
Mol. Phys. **107**, 1209 (2009).
23. Carpenter B. K., Pittner J., Veis L.:
Ab Initio Calculations on the Formation and Rearrangement of Spiropentane
J. Phys. Chem. A **113** 10557–10563 (2009).
24. Bhaskaran-Nair K., Demel O., Pittner J.:
Multireference Mukherjee's Coupled Cluster method with triexcitations in the linked formulation: Efficient implementation and applications
J. Chem. Phys. **132**, 154105 (2010).
25. Demel O., Bhaskaran-Nair K., Pittner J.:
Uncoupled multireference state-specific Mukherjee's coupled cluster method with triexcitations
J. Chem. Phys. **133**, 134106 (2010).
26. Bhaskaran-Nair K., Demel O., Šmydke J., Pittner J.:
Multireference State-Specific Mukherjee's coupled cluster method with non-iterative triexcitations using uncoupled approximation
J. Chem. Phys., **134**, 154106 (2011).
27. Šimsa D., Demel O., Bhaskaran-Nair K., Hubač I., Mach P., Pittner J.:
Multireference Coupled Cluster Study of the Oxyallyl Diradical
Chem. Phys. **401**, 203 (2012).

Statement about the authorship of the presented publications: In the majority of the presented publications the contribution of the author of this Thesis was pivotal, contributing either by development of the theory, its computer implementation, or supervising a student who was performing numerical calculations in the application-oriented papers. This is reflected by the fact that he was the corresponding author of 17 publications and the first author of 11 publications (with overlap). His role in the remaining publications was also essential. This is further detailed in a separate document submitted with the application.

Appendix B: List of publications by J. Pittner

Scientometric data

Number of papers registered in Web of Science: **76**

Total number of citations: **2037**

Total number of citations without self-citations: **1598**

Current H-index: **26**

Scientific journal papers

1. Dugourd Ph., Blanc J., Bonačić-Koutecký V., Broyer M., Chevaleyre J., Koutecký J., Pittner J., Wolf J.-P., Wöste L.:
Competition between Planar and Nonplanar Structure in Alkali Hexamers: The Example of Li_6 ,
Phys. Rev. Lett. **67**, 2638–2641 (1991)
2. Bonačić-Koutecký V., Pittner J., Scheuch C., Guest M. F., and Koutecký J.:
Quantum Molecular Interpretation of the Absorption Spectra of Na_5 , Na_6 and Na_7 Clusters,
J. Chem. Phys. **96**, 7938–7958 (1992)
3. Bonačić-Koutecký V., Fuchs C., Pittner J., and Koutecký J.:
Theoretical Interpretation of Optical Response Properties of Simple Metal Clusters,
Ber. Bunsenges. Phys. Chem. **96**, 1262–1270 (1992)
4. Bonačić-Koutecký V., Fantucci P., Fuchs C., Koutecký J., and Pittner J.:
Nature of Excitations in Small Alkali Metal and other Mixed Clusters,
Z. Phys. D **26**, 17–22(1993)
5. Bonačić-Koutecký V., Fuchs C., Gaus J., Pittner J., and Koutecký J.:
Ground and Excited States Properties of $Na_4F_{m=1-3}$, Li_4H , and Li_4H_2 Clusters,
Z. Phys. D **26**, 192–194 (1993)
6. Bonačić-Koutecký V., Fantucci P., Fuchs C., Gatti C., Pittner J., and Polezzo S.:
Ab Initio Predictions of Optically Allowed Transitions in Na_{20} ; Nature of Excitations and Influence of Geometry
Chem. Phys. Lett., **213**, 522–526 (1993)
7. Bonačić-Koutecký V., Češpiva L., Fantucci P., Pittner J., and Koutecký J.:
Effective Core Potential – Configuration Interaction Study of Electronic Structure and Geometry of Small Anionic Ag_n Clusters; Predictions and Interpretation of Photodetachment Spectra
J. Chem. Phys., **100**, 490–506 (1994)
8. Bonačić-Koutecký V., Češpiva L., Fantucci P., Fuchs C., Guest M.F., Koutecký J., and Pittner J.:
The Geometric Structures and Optical Response Properties of Small Na_nMg Clusters
Chem. Phys. **186**, 275–287 (1994)
9. Bonačić-Koutecký V., Češpiva L., Fantucci P., Fuchs C., Koutecký J., and Pittner J.:
Quantum Chemical Interpretation of Optical Response of Small Metal Clusters
Comments Atomic Mol. Phys. **31**, 233–290 (1995)

10. Vezin B., Dugourd Ph., Bordas C., Rayane D., and Broyer M., Bonačić-Koutecký V. and Pittner J., Fuchs C., Gaus J., Koutecký J.:
Electronic properties and geometric structures of Li_4H and Li_9H from optical absorption spectra
J. Chem. Phys., **102**, 2727–2736 (1995)
11. Bonačić-Koutecký V., Pittner J., Fuchs C., Fantucci P., Guest M. F., Koutecký J.:
Ab-initio Predictions of Structural and Optical Properties of Na_n^+ Clusters; Interpretation of Depletion Spectra at Low Temperature
J. Chem. Phys **104**, 1427–1440 (1996)
12. Bonačić-Koutecký V., Pittner J., Koutecký J.:
Ab-initio study of structural and optical response properties of excess-electrons in lithium-hydride and sodium-fluoride clusters.
Chem. Phys. **210**, 313–341 (1996)
13. Deutsch H., Becker K., Pittner J., Bonačić-Koutecký V., Matt S., and Märk T. D.:
Semi-Classical Calculations of the Cross Section for Electron-Impact Ionization of C_{60} .
J. Phys. B **29**, 5175–5181 (1996)
14. Bonačić-Koutecký V., Pittner J., Pou-Amerigo R., Hartmann M.:
Ab-initio study of structural and optical properties of nonstoichiometric alkalimetal-oxides
Z. Phys. **D40**, 445–447 (1997)
15. Bonačić-Koutecký V., Pittner J., Koutecký J.:
Ab-initio study of optical response properties of nonstoichiometric lithium-hydride and sodium-fluoride clusters with one- and two-excess electrons
Z. Phys. **D40**, 441–444 (1997)
16. Bonačić-Koutecký V., Pittner J.:
Ab-initio study of optical response properties of nonstoichiometric lithium-hydride and sodium-fluoride clusters
Chem. Phys. **225**, 173–187 (1997)
17. Hartmann M., Pittner J., Bonačić-Koutecký V., Heidenreich A., Jortner J.:
Theoretical exploration of femtosecond multi state nuclear dynamics of small clusters
J. Chem. Phys. **108**, 3096–3113 (1998)
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Ultrafast Dynamics of Small Clusters on the Time Scale of Nuclear Motion
J. Phys. Chem. **A 102**, 4069–4074 (1998)
19. Bonačić-Koutecký V., Reichardt D., Pittner J., Fantucci P., Koutecký J.:
Ab Initio Molecular Dynamics for Determination of Structures of Alkali Metal Clusters and Their Temperatures Behavior. Example of Li_9^+ .
Coll. Czech. Chem. Comm. **63**, 1431–1446 (1998)
20. Bonačić-Koutecký V., Pittner J., Reichardt D., Fantucci P., Koutecký J.:
Quantum Chemical Study of Electronic and Dynamic Properties of Metal and Mixed Non-stoichiometric Clusters
Czech. J. Phys. **48**, 637–658 (1998)

21. Bonačić-Koutecký V., Pittner J., Boiron M., Fantucci P., Koutecký J.:
An accurate relativistic effective-core-potential for excited states of Ag-atom; Application to study of the absorption spectra of Ag_n and Ag_n⁺ clusters
J. Chem. Phys. **110**, 3876–3886 (1999)
22. Pittner J., Nachtigall P., Čárský P., Mášik J., Hubač I.:
Assessment of the single-root multireference Brillouin–Wigner CCSD theory. Test calculations on CH₂, SiH₂, and twisted ethylene.
J. Chem. Phys., **110**, 10275–10282 (1999)
23. Deutsch H., Pittner J., Bonačić-Koutecký V., Becker K., Matt S., Märk T. D.:
Theoretical determination of the absolute electron impact ionization cross sections for silver clusters Ag_n (n = 2–7).
J. Chem. Phys., **111**, 1964–1971 (1999)
24. Bonačić-Koutecký V., Boiron M., Pittner J., Fantucci P., Koutecký J.:
Structural and optical properties of small neutral and charged pure and oxidized silver clusters
Eur. Phys. J. **D 9**, 183–187 (1999)
25. Hartmann M., Pittner J., van Dam H., Bonačić-Koutecký V.:
Theoretical study of femtosecond pump–probe signals of nonstoichiometric alkali halide clusters
Eur. Phys. J. **D 9**, 393–397 (1999)
26. Hubač I., Pittner J., Čárský P.:
Size-extensivity correction for the state-specific multireference Brillouin–Wigner coupled-cluster theory
J. Chem. Phys., **112**, 8779–8784 (2000)
27. Sancho-García J. C., Pittner J., Čárský P., Hubač I.:
Multireference coupled-cluster calculations on the energy of activation in the automerization of cyclobutadiene: assessment of the state-specific multireference Brillouin–Wigner theory
J. Chem. Phys., **112**, 8785–8788 (2000)
28. Hartmann M., Pittner J., van Dam H., Veyret V., Bonačić-Koutecký V.:
Theoretical Exploration of Stationary and of Ultrafast Spectroscopy of Small Clusters
Appl. Phys. B **71**, 343–349 (2000)
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Ab initio three dimensional quantum dynamics of Ag₃ clusters in the NeNePo process
Chem. Phys. Lett. **318**, 256–262 (2000)
30. Pittner J., Jungwirth P.:
Potential energy curves for the ground and low-lying excited states of IBr calculated with relativistic effective core potentials and spin-orbit interactions.
Chem. Phys. Lett., **321**, 281–286 (2000)

31. Hartmann M., Pittner J., Bonačić-Koutecký V.:
Ab-Initio Adiabatic Dynamics Involving Excited States Combined with Wigner Distribution Approach to Ultrafast Spectroscopy Illustrated on Alkali Halide Clusters
J. Chem. Phys., **114**, 2106–2122 (2001)
32. Hartmann M., Pittner J., Bonačić-Koutecký V.:
Ab initio nonadiabatic dynamics involving conical intersection combined with Wigner distribution approach to ultrafast spectroscopy illustrated on Na₃F₂ cluster
J. Chem. Phys., **114**, 2123–2136 (2001)
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A multireference coupled cluster study of the singlet-triplet gap in tetramethylenethane molecule
J. Phys. Chem. **A** **105**, 1354–1356 (2001)
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Int. J. Quant. Chem. **84**, 714–739 (2001)
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State-specific Brillouin-Wigner multireference coupled cluster study of the F₂ molecule: Assessment of the a posteriori size-extensivity correction
J. Molec. Struc. (Theochem) **547**, 239–244 (2001)
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Theoretical exploration of ultrafast spectroscopy of small clusters
Europ. Phys. J., **D** **16**, 133–138 (2001)
37. Pittner J., Demel O., Čársky P., Hubač I.:
Four-reference state-specific Brillouin-Wigner coupled-cluster method: Study of the IBr molecule.
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