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DRESSING OF INTERACTION VERTICES  
IN MULTI-REFERENCE  
COUPLED CLUSTER THEORY

Theses of the Ph.D. dissertation

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## Introduction

Over the last decades, a wealth of physical-chemical information and understanding has been gained with the help of electronic structure calculations. Although the electronic Schrödinger equation cannot be solved exactly (except for very simple systems), remarkably accurate approximate solutions are available as long as correlation (entanglement) of electrons is weak. Hartree-Fock-type mean field methods employing a single Slater determinant, with perturbative or Coupled Cluster (CC) corrections built on them are often able to reproduce properties of weakly correlated atomic-molecular systems with experimental accuracy.

Unfortunately, as the correlation of electrons becomes stronger (molecules with dissociating covalent bonds being common examples), these methods tend to become unreliable. In such strongly correlated settings, multi-determinantal (Multi-Reference, MR) wave functions must be used instead of a single determinant to obtain a qualitatively good description of the system. For accurate results, however, MR wave functions need further corrections, either perturbative or CC-type. There is no unique way to define the MR generalization of the CC approach, and multiple different MRCC models have been proposed over the years. While MRCC methods have often had impressive success in the treatment of strong correlation, there are still many problems left to solve.

So-called internally contracted MRCC (ic-MRCC) methods form a conceptually and computationally appealing family of MRCC methods. In their simple parametrization, a single exponential wave operator acts on the whole multi-determinantal reference function instead of different operators acting on each determinant. This makes development of theories (in principle) much simpler compared to other MRCC Ansätze.

Analytical and numerical studies concerning the ic-MRCC theory form the focus of my Ph.D. dissertation.

## Overview

The starting point of my electronic structure model is the normal ordered ic-MRCC parametrization of Mukherjee et al.<sup>1</sup>. Derivations are carried out with the help of the MR generalization of operator normal ordering and the corresponding Wick theorem, as developed by Kutzelnigg and Mukherjee<sup>2</sup>. The novelty of my approach compared to previous ic-MRCC models lies in the introduction of the so-called dressed interaction vertices. Dressed one- and two-body interaction vertices formally resemble the ("bare") Fockian and electron-electron interaction vertices of a single determinantal theory. They can be used as building blocks in the development of MRCC theories similarly to the way their bare counterparts are used to construct single determinantal CC theories. However, dressed vertices are functions of so-called density cumulants (which carry the correlation content of the multi-determinantal reference), and for this reason, they are more suitable for strongly correlated scenarios. Working with dressed vertices makes the otherwise complicated derivations of the ic-MRCC

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<sup>1</sup>Mahapatra, Datta, Bandyopadhyay, Mukherjee; *Adv. Quantum Chem.* **30** 163 (1998)

<sup>2</sup>Kutzelnigg, Mukherjee, *J. Chem. Phys.* **107** 432 (1997)

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equations considerably easier. Construction and plausible interpretation of dressed vertices are facilitated by Goldstone diagrammatic techniques.

Development and numerical assessment of the above ic-MRCC approach are the main results of my dissertation (discussed in Chapters 3-6. and Appendices C-E).

## Results

1. I demonstrated how dressed interaction vertices naturally arise in the derivation of the ic-MRCC equations. I proposed simple algebraic and diagrammatic approaches for the general construction of the various dressed interaction vertices, and used similar methods to construct the general ic-MRCC formalism with their help (result of Ref. T1.).
2. I used a diagrammatic expansion formally resembling the many-body perturbation series to show how dressed interaction vertices contribute to CC amplitudes and to the energy correction. Based on this analysis, I proposed a partitioning of electron correlation into intra- and intervertex parts, the intravertex part being described by the cumulant dressing of vertices, and the intervertex part taken into account by cumulant couplings between vertices (result of Ref. T1.).
3. I used the diagrammatic analysis of amplitudes and energy to define four simple approximation schemes to the general ic-MRCC framework. The first three schemes take only the intravertex part of electron correlation into account: these are idCCSD and two further ring-type approximations, referred to as rmCCD and rCCD(UGA). In the more involved idCCSD+ $\lambda$ F model, intervertex electron correlation is also treated to some degree (results of Refs. T1. and T3.).
4. As a detour in weakly correlated phenomena, I investigated how ic-MRCC accounts for dispersion interactions. I showed the emergence of the London dispersion formula for the (formally) second-order approximation of the idCCSD energy. In this special case, I gave a simple expression for the dispersion coefficient in terms of quantities formally resembling frequency-dependent polarizabilities (result of Ref. T2.).
5. I implemented all of the above approximate ic-MRCC methods in the Budapest version of the MUNGAUSS quantum chemistry package, to be used as correction methods for a simple geminal wave function called GVB (Generalized Valence Bond).
6. The elementary excitations used for the ic-MRCC calculations form a linearly dependent set of vectors; this redundancy must be treated in order to avoid possible numerical instabilities. In order to tackle this problem, I adopted a redundancy handling approach developed in signal theory, based on the so-called frame vectors. The algorithm was implemented by me in the same quantum chemistry program.
7. I assessed the quality of the proposed approaches by performing calculations on strongly correlated systems (published in Refs. T1. and T3.). Examples of strongly correlated

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systems included the single and double bond dissociation of the H<sub>2</sub>O molecule and the triple bond dissociation of N<sub>2</sub>. The results showed GVB-rmCCD to be the most accurate approximation in quantitative terms, as compared to FCI benchmark values. On the other hand, GVB-idCCSD+ $\lambda$ F has proven to be the most correct in qualitative terms.

8. As a further test case, I performed calculations for the BeH<sub>2</sub>  $\rightarrow$ Be+H<sub>2</sub> reaction pathway. In this example GVB-idCCSD proved to be the most reliable approach, with GVB-rCCD(UGA) seriously lagging behind. However, none of our methods performed particularly well compared to other MRCC approaches in the literature (published in Refs. T1. and T3.).
9. I further assessed the performance of the GVB-rCCD(UGA) method on weakly correlated systems. The examples included the calculation of conformational barriers for H<sub>2</sub>O, NH<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, deprotonation energies of H<sub>2</sub>O and CH<sub>3</sub>OH, and dispersion interactions of He and Ne dimers. The results showed a considerable improvement over GVB in all of the above test cases, and were in many cases closely comparable with the benchmark CCSD(T) energies (published in Refs. T2. and T3.).

## Publications supporting the thesis

- T1. Á. Margócsy, Á. Szabados: Dressing of Vertices by Cumulants in Multi-Reference Coupled Cluster; *Journal of Chemical Theory and Computation* **17** 11 6947 (2021)  
DOI: <https://doi.org/10.1021/acs.jctc.1c00730>
- T2. Á. Margócsy, Á. Szabados: Calculation of dispersion interactions with the geminal-based ring Coupled Cluster Doubles method; *Theoretical Chemistry Accounts* **139** 150 (2020)  
DOI: <https://doi.org/10.1007/s00214-020-02657-1>
- T3. Á. Margócsy, Á. Szabados: Ring coupled cluster doubles at the multireference level; *The Journal of Chemical Physics* **152** 204114 (2020)  
DOI: <https://doi.org/10.1063/5.0005075>

## Further publications

- O1. Zs. É. Mihálka, M. Nooijen, Á. Margócsy, Á. Szabados, P. R. Surján: The  $\gamma$  function in quantum theory II. Mathematical challenges and paradoxa; *Journal of Methemathical Chemistry* **60** 267 (2022)  
DOI: <https://doi.org/10.1007/s10910-021-01311-w>
- O2. Zs. É. Mihálka, Á. Margócsy, Á. Szabados, P. R. Surján: On the variational principle for the non-linear Schrödinger equation; *Journal of Methemathical Chemistry* **58** 340

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(2019)

DOI: <https://doi.org/10.1007/s10910-019-01082-5>

O3. Á. Margócsy, P. Kowalski, K. Pernal, Á. Szabados: Multiple bond breaking with APSG-based correlation methods: comparison of two approaches; *Theoretical Chemistry Accounts* **137** 159 (2018)

DOI: <https://doi.org/10.1007/s00214-018-2355-4>

O4. Á. Szabados, Á. Margócsy: Ring coupled-cluster doubles correction to geminal wavefunctions; *Molecular Physics* **115** 2731 (2017)

DOI: <https://doi.org/10.1080/00268976.2017.1317111>