An Alternative Algebraic Framework for the Simplification of Coupled Cluster Type Expectation Values

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»*'Drink up.' He added, perfectly factually: 'The world's about to end.'* [. . .] *'This must be Thursday,' said Arthur to himself, sinking low over his beer, 'I never could get the hang of Thursdays.'*«

Dialog between Ford Prefect and Arthur Dent,
in 'The Hitchhikers Guide to the Galaxy' by Douglas Adams.

Meinen Eltern

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Kurzzusammenfassung

Das Coupled-Cluster-Verfahren zählt zu den am häufigsten angewandten und effizientesten Korrelationsverfahren in der Quantenchemie. Insbesondere die CCSD(T)-Näherung, in der der Cluster-Operator auf Einfach- und Zweifachsubstitutionen (**S**ingles und **D**oubles) der Referenzdeterminante beschränkt wird und die störungstheoretische Dreifachanregungsenergie (**T**riples) addiert wird, ist zum Standard der Quantenchemie geworden. Allerdings beschränkt sich diese Methode aufgrund ihrer ungünstigen Skalierung (N^7, wobei N der Anzahl der Basisfunktionen entspricht) auf vergleichsweise kleine Systeme. Für die volle Behandlung der Dreifachanregungen skaliert der Rechenaufwand bereits mit N^8, für jeden weiteren Anregungsgrad erhöht sich der Exponent um weitere zwei.

Durch diese Arbeit soll es möglich werden, die Rechenzeit für beliebige Anregungsgrade im Falle geschlossener Elektronenschalen zumindest um einen mit steigendem Anregungsgrad wachsenden Faktor zu reduzieren. Hierzu wird davon ausgegangen, dass der Raumteil jeweils zweier Spinorbitale gleich ist, sodass in den Anregungen die beiden möglichen Spinzustände gleich behandelt werden können. Während die dadurch entstehenden Restriktionen für die Cluster-Amplituden im CCSD noch durch einfache Spinintegration konstruiert werden können, müssen die Einschränkungen für höhere Anregungen über die Betrachtung der Raumorbitalanregungsoperatoren $\hat{E}$ hergeleitet werden.

Im ersten Teil der Arbeit wird ein allgemeines Schema zur Konstruktion der spingemittelten Cluster-Amplituden und Projektionsgleichungen zu deren numerischer Bestimmung entwickelt, das über die CCSD-Näherung hinaus geht. Der zweite Teil der Arbeit besteht aus der Implementierung der Ergebnisse des ersten Teils in einen schon bestehenden effizienten CC-Programmcode.

Abstract

The Coupled-Cluster (CC) method is one of the most popular and efficient correlation methods in quantum chemistry. Especially the CCSD(T) approximation, which includes single and double excitations by means of the application of the cluster operator to a reference determinant and triple excitations via a perturbative treatment, has become a standard tool in quantum chemical applications. However, the method is restricted to relatively small system sizes due to its unfavourable scaling (N^7, where N is the number of basis functions applied). For the full treatment of triple excitations the scaling advances to N^8 and every further excitation level increases the exponent by two.

The goal of this work is to reduce the calculation time for closed shell systems at least by a factor growing with the excitation level for arbitrary truncation levels. This is done by restricting the spatial parts of the spin orbitals and thus treat pairs of spin orbitals on the same footing. The restrictions can be easily constructed for the CCSD model by spin integration. The derivation of the restrictions arising in higher excited case will be done employing the spatial orbital excitation operators $\hat{E}$.

In the first part of this work an algorithm is derived that is capable of the derivation of the energy and amplitude equations for arbitrary excitation levels. In the second part an implementation of this algorithm is presented.

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Chapter 1

Introduction

Contents

1.1 Historical Notes

The coupled cluster (CC) method was invented by Coester and Kümmel [1, 2] in the late 1950s as a method for nuclear physics. However, the inventors regarded their method as inapplicable in their field. In 1966 Čížek [3, 4, 5] introduced the CC theory in quantum chemistry as *coupled pair many electron theory* (CPMET).

1.1.1 The Coupled Pair Many Electron Theory

In his ansatz Čížek applied an exponential wave operator including all powers of double substitution operators, by means of its Taylor expansion, to the ground state Slater-determinant and evaluated algebraic equations in terms of powers of the coefficients (amplitudes) of the substituted determinants. In his approach he employed both the spin orbital and the spatial orbital framework.

1.2 State of the Art in Coupled Cluster Theory

Despite its high computational complexity coupled cluster theory emerged into a widely used tool for computational chemists [6, 7, 8]. In particular truncated versions of the theory, namely coupled cluster singles and doubles (CCSD) and its perturbationally augmented form (CCSD(T)) [9], have become popular and are implemented in many *ab* *initio* electronic structure program codes such as MOLPRO [10], MOLCAS [11] or TURBOMOLE [12].

Especially the CCSD(T) ansatz emerged as the gold standard of quantum chemistry for energies as well as properties including dipole moments, gradients [13] or chemical shifts for nuclear magnetic resonance spectroscopy [14, 15, 16, 17].

1.2.1 Truncated Versions of the Theory

A hierarchy of methods with increasing accuracy and complexity has evolved in the past. The truncation of the cluster operator at different substitution levels leads to a series of methods which produce energies that converge to the full configuration interaction (FCI) limit in a very fast way (i.e. substantially faster than the configuration interaction series of methods). Implementations for various truncation levels are known, such as CCSDT [18, 19, 20], CCSDTQ [21] and CCSDTQP [22, 23].

Due to the high complexity of both the derivation as well as the solution of the algebraic equations defined by the setup of the CC ansatz, implementations often restrict themselves to truncated versions of the theory. The program package MOLPRO for example can only handle up to double excitations in the cluster operator. Even triple excitations are handled on a perturbational level only. Up to now, the author is aware of only a few codes capable of the generation and solution of general order coupled cluster equations with the correct scaling [24, 25, 26, 27, 28, 29].

1.2.2 Multi Reference Generalizations of the Theory

In contrast to the configuration interaction (CI) method[1], a multi reference genraliztion of the coupled cluster ansatz is neither straightforward nor unique and mainly two different classes of approaches have been developed. The first one is the valence universal method of Mukherjee and co-workers [30, 31, 32, 33, 34], the second one is the state universal approach of Jeziorski and Monkhorst [35, 36, 37, 38, 39, 40], which at the moment has a huge number of so-called state specific variants [41, 42, 43, 44].

Both original ansätze showed to be not very accurate, since in their working equations the expansion coefficients (amplitudes) are shared for several states. This leads to a smaller flexibility of the wavefunction per state. Furthermore, especially for many reference states the possibility of diverging cluster operators is given, commonly known as the intruder state problem.

These are the reasons for the development of the state specific ansätze mentioned above. However, research in this field is still in progress. Presently, the author is not aware of a genuine multi reference coupled cluster ansatz that is truly satisfactory, meaning a method combining the properties of the single reference coupled cluster ansatz with a true generalization to more than one reference wavefunction.

[1] The configuration interaction method employs a linear expansion of the wavefunction in the many particle basis set. For details see sec. 2.2.2.1.

1.3 Scope of This Work

The following section contains an overview over the goals of this work. It has mainly two aspects, namely a theoretical and an implementational, which will be dealt with separately. A final chapter will discuss the numerical testing of the concepts and the implementation presented.

Table 1.1: Construction of triples amplitudes from linear combinations of spin independent amplitudes. Calculation via a linear equation system employing the blue colored amplitudes. The amplitudes are taken from a CCSDT calculation of the Li_2 molecule at an interatomic distance of 3.5 a.u. employing a 6-31Gp basis set [45].

Amplitude	Determinant	$\hat{E}$-Operator Combination	
0.00001534	$\lvert\bar{1}\bar{2}\bar{3}456\rangle$	0.000025286	$\hat{E}_1^{\perp}\lvert 0\rangle$
-0.00000980	$\lvert\bar{1}\bar{2}3\bar{4}56\rangle$	-0.000001483	$\hat{E}_2^{\perp}\lvert 0\rangle$
-0.00000112	$\lvert\bar{1}\bar{2}34\bar{5}6\rangle$	0.000030452	$\hat{E}_3^{\perp}\lvert 0\rangle$
-0.00000443	$\lvert\bar{1}\bar{2}345\bar{6}\rangle$		
-0.00001528	$\lvert\bar{1}2\bar{3}\bar{4}56\rangle$	-0.000008973	$\hat{E}_4^{\perp}\lvert 0\rangle$
0.00000012	$\lvert\bar{1}2\bar{3}4\bar{5}6\rangle$	-0.000018799	$\hat{E}_5^{\perp}\lvert 0\rangle$
-0.00000018	$\lvert\bar{1}2\bar{3}45\bar{6}\rangle$		
0.00001074	$\lvert\bar{1}23\bar{4}\bar{5}6\rangle$		
0.00001434	$\lvert\bar{1}23\bar{4}5\bar{6}\rangle$		
-0.00000973	$\lvert\bar{1}234\bar{5}\bar{6}\rangle$		
0.00000973	$\lvert 1\bar{2}\bar{3}\bar{4}56\rangle$		
-0.00001434	$\lvert 1\bar{2}\bar{3}4\bar{5}6\rangle$		
-0.00001074	$\lvert 1\bar{2}\bar{3}45\bar{6}\rangle$		
0.00000018	$\lvert 1\bar{2}3\bar{4}\bar{5}6\rangle$		
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0.00001528	$\lvert 1\bar{2}34\bar{5}\bar{6}\rangle$		
0.00000443	$\lvert 12\bar{3}\bar{4}\bar{5}6\rangle$		
0.00000112	$\lvert 12\bar{3}\bar{4}5\bar{6}\rangle$		
0.00000980	$\lvert 12\bar{3}4\bar{5}\bar{6}\rangle$		
-0.00001534	$\lvert 123\bar{4}\bar{5}\bar{6}\rangle$		

1.3.1 Motivation

There are many efficient coupled cluster implementations existing already. Most of these implementations include at most doubles substitutions (and perturbational triples). The probably fastest implementation of a closed shell CCSD code at the moment is included in the MOLPRO program package.

Table 1.2: Independent operators and number of singlet spin functions for different excitation levels and numbers of open shells.

level	open shells	$\#\hat\tau$	$\hat\eta$-operators	$\#\hat\eta$	$f(N,S=0)$
1-fold	2	2	$\hat\eta_i^a$	1	1
2-fold	0	1	$\hat\eta_{ii}^{aa}$	1	1
	2	2	$\hat\eta_{ii}^{ab}$	1	1
	4	6	$\hat\eta_{ij}^{ab}, \hat\eta_{ji}^{ab}$	2	2
3-fold	2	2	$\hat\eta_{iij}^{aab}, \hat\eta_{jii}^{aab}$	2	1
	4	6	$\hat\eta_{ijk}^{aab}, \hat\eta_{kij}^{aab}, \hat\eta_{jki}^{aab}$	3	2
		6	$\hat\eta_{iik}^{abc}, \hat\eta_{kii}^{abc}, \hat\eta_{iki}^{abc}$	3	2
	6	20	$P(ij)\left(\hat\eta_{ijk}^{abc}, \hat\eta_{kij}^{abc}, \hat\eta_{jki}^{abc}\right)$	6	5
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
n-fold	$2(n-k)$	$\binom{2(n-k)}{n-k}$		$(n-k)!$	$\frac{1}{1+n-k}\binom{2(n-k)}{n-k}$

It is however noteworthy that no implementation of a closed shell spin independent coupled cluster code for arbitrary substitution levels exists, but very recently Stanton and Gauss reported the implementation of spin intependent versions of CCSDT and CCSDTQ [46, 47]. It is the scope of this work to develop an algebraic term simplification capable of the derivation of spin independent coupled cluster equations for arbitrary substitution levels.

Upon inspection of the amplitudes (i.e. the expansion coefficients in the many body basis set) obtained from a spin orbital coupled cluster program applied to a closed shell reference (tab. 1.1), it is clear that a lot of memory and time could be saved by the application of a spin independent code. Table 1.1 shows that e.g. the twenty spin orbital based amplitudes, resulting from a spin orbital based calculation of the Lithium dimer, can be constructed out of *five* spin independent non-redundant amplitudes only (originating from the application of the orthogonalized spin independent operators $\hat{E}_i^{\perp}$ in the CC framework). This implies that the size of this part of the amplitude tensor as well as the residual tensor is in the spin independent case only one fourth of the original size. This results in an reduction in computational time of an even greater magnitude.

It is obvious that the ratio between the number of spin orbital based amplitudes and spin independent amplitudes grows with the maximal substitution level since the number of linear independent spin eigenfunctions does not grow as rapidly as the number of primitive spin functions as well as the number of substitution operators (see also tab. 1.2).

Table 1.3: Typesetting of mathematical objects throughout this work.

Object	Symbol
Scalar	d
Vector	$\vec{d}$
Matrix	$\mathbf{D}$
Quantum Mechanical Operator	$\hat{d}$
Mathematical Operator	d
Field/Linear Space	$\mathbb{D}$(or $\mathbb{d}$)
(Lie-)Algebra	$\mathfrak{d}$(or $\mathfrak{D}$)

1.3.2 Theoretical Aspects

In the theoretical part of this work an alternative algebraic term simplification for coupled cluster type expectation values that has been developed is described. This new method relies on well known commutator relations for second quantized substitution operators and employs their characteristics as members of a Lie algebra.

1.3.3 Implementational Aspects

For the implementation of the algebraic term simplification several parts of the Quantum Objects Library (QOL, a program package used and developed by our group, initiated by Hanrath) had to be modified. Additionally, many new concepts and classes had to be implemented from scratch.

1.4 Technical and Notational Remarks

Throughout this work a consistent notation will be used. Scalar and vector (additionally marked by an over-rightarrow) quantities as well as quantum mechanical operators (additionally marked by a hat) are typeset in italic, matrices are typeset in boldface font. Mathematical operators, such as the differential operator, are typeset in an upright font.

Additionally there are several algebraic structures that have their own type: Fields and sometimes linear spaces are typeset in blackboard font whereas groups and algebras, especially Lie algebras, are typeset in fracture font.

It should be noted that, despite not fullfilling the criteria for a linear space, basis sets are commonly called spaces in the literature. This notation will be adopted in this work and thus basis sets are also typed in blackboard font for convenience.

Many, more or less convenient, fixed notations for distinct objects in many body theory have evolved in literature over time. In this work most of these conventions will be adapted. Table 1.4 gives an overview over the most common conventions.

It should be noted that lower case symbols refer to one particle quantities while upper case symbols refer to many particle quantities, e.g. $|\phi\rangle$ for a spatial orbital and $|\Phi\rangle$ for a

Table 1.4: Conventions for the notation of special objects in many body theory.

Object	Notation/Symbol
Hamiltonian	$\hat{H}$
Laplacian	Δ
Lagrangian	$\mathcal{L}$
Spin orbital	χ
Spatial Orbital	ϕ
Occupied Orbital Indices	$i, j, \ldots$
Virtual Orbital Indices	$a, b, \ldots$
Arbitrary Orbital Indices	$p, q, \ldots$
Space of Occupied Orbitals	$\mathbb{O}$
Space of Virtual Orbitals	$\mathbb{V}$
Entire Space of Orbitals	$\mathbb{W} = \mathbb{O} \cup \mathbb{V}$
Slater Determinant	$\vert\Phi\rangle$
-Ground State	$\vert\Phi_0\rangle$
-Substituted	$\vert\Phi_{ij\ldots}^{ab\ldots}\rangle$
Correlated Wavefunction	$\vert\Psi_{\text{method}}\rangle$
Configuration Interaction Coefficients[a)]	$c_{ij\ldots}^{ab\ldots}$
Coupled Cluster amplitudes[a)]	$t_{ij\ldots}^{ab\ldots}$
One Particle Operator Matrix Element	$\langle p\vert f\vert q\rangle$ or f_p^q
Two Particle Operator Matrix Element[a)]	$\langle pq\vert v\vert rs\rangle$ or v_{pq}^{rs}
General Substitution Operator	$\hat{\sigma}_{pq\ldots}^{rs\ldots}$
Spin Orbital Substitution Operator	$\hat{\tau}_{pq\ldots}^{rs\ldots}$
Spatial Substitution Operator	$\hat{\eta}_{pq\ldots}^{rs\ldots}$
Spin Orbital Compound Operator	$\hat{T}$
Spatial Orbital Compound Operator	$\hat{E}$

[a)] Symmetry issues concerning the indices of the many particle operator matrix elements are discussed when necessary. In general no special symmetry is assumed for the matrix elements.

Slater determinant. This rule applies only for symbols where a differentiation between the one and many body cases is necessary.

Finally, in chapter four a notation distinguishing between spin and spatial orbital indices is introduced. In this notation α and *beta* spin oprbital indices are described by under- and overbars, respectively. A detailed introduction to this notation is postponed to the beginning of chapter four.

Chapter 2

Introductory Theory

Contents

This chapter contains a description of the central problem of quantum chemistry, i.e. the many body interaction of electrons in the potential provided by the positive charge of atomic nuclei [48]. After the description of the problem, the wavefunction based approach to the approximate solution of this problem is discussed. Herein the focus will lie on the description of electronic correlation methods, mainly configuration interaction and coupled cluster. The discussion of the coupled cluster formalism then leads to the main topic of this work, namely the setup of an algebraic framework for the derivation of spin independent coupled cluster equations.

The concepts described in this chapter are well known and included in many popular quantum chemistry textbooks, e.g. [49, 50, 51, 52, 53, 54].

2.1 The Electronic Structure Problem

The main problem electronic structure theory has to deal with is the pairwise repulsive electrostatic interaction of electrons. Approximations addressing this challenge will be formally described in the following sections.

2.1.1 The Schrödinger Equation

The quantum mechanical description of a system (assumed stationary over time) in a non-relativistic framework is provided by the time independent SCHRÖDINGER equation 2.1 [55, 56, 57, 58]:

$$\hat{H}\Psi = E\Psi \ . \tag{2.1}$$

Herein the wavefunction Ψ describes the considered system, $\hat{H}$ the Hamiltonian, containing operators for its kinetic and potential energy and E the energy of a valid state of the system.

Since the kinetic energy operator contains second derivatives of the wavefunction with respect to particle coordinates, the SCHRÖDINGER equation has to be considered a partial differential equation of second order.

2.1.2 The Electronic Hamiltonian

The nuclei of a polyatomic system can be seen as quasi-stationary entities due to their mass which is at least three orders of magnitude greater than that of an electron. This results, assuming an evenly distributed kinetic energy, in a much smaller velocity and subsequently only a marginal contribution to the kinetic energy.

According to this analysis, first carried out by BORN and OPPENHEIMER [59], a major simplification of the Hamiltonian can be achieved by neglecting the kinetic energy operators regarding the nuclei. Furthermore the potential energy arising from the repulsion between nuclei can be evaluated via the classical COULOMB law by insertion of their fixed positions.

The preceding discussion gives rise to an electronic Hamiltonian $\hat{H}_{\text{el}}$ as described in eq. 2.2[1],

$$\hat{H}_{\text{el}} = -\frac{1}{2}\sum_i \Delta_i - \sum_{iI} \frac{Z_I}{r_{iI}} + \sum_{i<j} \frac{1}{r_{ij}} \ , \tag{2.2}$$

where i, j are indices for electrons and I is the index for nuclei. Z_I is the charge of nucleus I and r is the distance of two particles. The LAPLACE operator Δ_i is defined by

[1] Throughout this work the convention of atomic units is used. In this framework, many constants occuring in quantum theory are set to unit values, e.g. $\hbar = e = m_e = a_0 = 4\pi\epsilon_0 = 1$.

$$\Delta_i = \vec{\nabla}_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \,, \tag{2.3}$$

where

$$\vec{r}_i = (x_i, y_i, z_i) \tag{2.4}$$

is the position vector of particle i.

2.1.3 Electron Correlation

Considering the last term of the electronic Hamiltonian in eq. 2.2, usually referred to as the inter-electronic Coulomb interaction, it is clear that the movement of the electrons is correlated.[2] A similar effect is known in the physics of planetary movement, where the motion of different planets is coupled via the gravitational law[3]. Closed form solutions to both problems are only existent for a few well conditioned cases, e.g. the coupled motion of two particles, the motion of one particle in a central spherical symmetric potential, and certain cases involving three particles with specific boundary conditions.

On the other hand, it can be shown that an analytical solution to the problem exists in form of a converging power series [60]. Even before this remarkable result it was an established procedure to expand the approximate wavefunction into a linear combination of basis functions. The following sections will give an overview over the most popular approaches of this type.

2.2 Wavefunction Based Approaches

Wavefunction based approaches approximate the exact wavefunction in a basis of suited analytical functions. In contrast, there are (semi-)empirical models which adjust certain quantities occuring in the calculation of a system (e.g. integrals) to experimental data. This type of approach will not be considered in this work.

2.2.1 The Independent Particle Model

As a crude first approximation it is possible to partition the electronic Hamiltonian into a sum of effective[4] one particle operators $\hat{h}_i$:

$$\hat{H}_{\mathrm{el}} = \sum_i \hat{h}_i \,. \tag{2.5}$$

[2] In the sense of mathematical correlation, i.e. the position of an electron is a function of the position of the other electrons. For correlation in Löwdin's sense cf. section 3.2.2.

[3] In fact the potentials of electrostatic as well as gravitational interaction show the same r^{-1} dependency .

[4] i.e. these operators may well be influenced by the structure of the other single particle wave-functions, cf. section 2.2.1.2.

It can be shown by simple algebraic manipulations that the eigenfunction of such an operator must be a product of eigenfunctions to the individual one particle operators. This product is known as the HARTREE product of the one particle functions. The one particle functions involved in this expansion are usually referred to as spin orbitals:

$$\begin{aligned} \chi_i : \mathbb{R}^3 \times \mathbb{S} &\to \mathbb{C} \\ (\vec{x}, \omega) &\mapsto \chi_i(\vec{x}, \omega) \,, \end{aligned} \tag{2.6}$$

where $\vec{x}$ are the spatial and ω is the spin coordinate of the particle ($\mathbb{S} := \{\alpha, \beta\}$).

2.2.1.1 Slater Determinants

There are two severe drawbacks of this single product wavefunction ansatz regarding the nature of electrons. First of all, as any elementary particles, electrons are indistinguishable, which the product wavefunction does not account for. The second drawback is due to the fermionic nature of the electrons. This requires the wavefunction to be antisymmetric with respect to the interchange of a pair of electrons. The only normalized, completely antisymmetric, n-linear form over a vector space (spanned by n orbitals) turns out to be the determinant (cf. e.g. [61], sec. 4.2). Thus, the wavefunction should be written as a so called SLATER determinant [62]:

$$|\Phi\rangle = \frac{1}{\sqrt{n!}} \det(\chi_i(j))_{i,j=1,\ldots,n} \,. \tag{2.7}$$

Herein χ_i denotes the ith spin-orbital and j is the coordinate vector of the jth electron.

Another, more formal way of writing a SLATER determinant is

$$|\Phi\rangle = \sqrt{n!}\mathcal{A} \prod_i^n \chi_i(i) \,, \tag{2.8}$$

where $\mathcal{A}$ is the antisymmetrizer, an idempotent operator defined by

$$\mathcal{A} = \frac{1}{n!} \sum_{\hat{P}_i \in \mathfrak{S}_n} (-1)^{p(\hat{P}_i)} \hat{P}_i \,. \tag{2.9}$$

The $\hat{P}_i$ are the permutation operators of n particles operating on the particle index. This variant in notation is commonly known as the LEIBNIZ expansion rule for determinants.

Since the determinant includes all permutations of the particle coordinates, one can easily see that the indistinguishability of the electrons in the probability density is now fulfilled. The parity $p(\hat{P}_i)$ of the ith permutation guarantees a sign change of the determinant when two electron coordinates are interchanged[5].

Since now the physical requirements for a non-interacting system of electrons are satisfied, the SLATER determinant is a common starting point for electronic structure calculations.

[5] This is in close analogy to the sign change of the determinant of a usual $n \times n$-matrix when two columns are swapped.

2.2.1.2 Hartree-Fock Approach

The HARTREE-FOCK approach [63, 64] results from minimizing the expectation value of the electronic Hamiltonian with respect to the variation of the spin orbitals in a single SLATER determinant:

$$E[\{|\chi_i\rangle\}] := \frac{\langle\Phi|\hat{H}_{\mathrm{el}}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \overset{!}{=} \min \ . \tag{2.10}$$

When additionally the constraint is considered that the spin orbitals are required to stay orthonormal the problem leads to the minimization of the Lagrangian:

$$\mathcal{L}[\{|\chi_i\rangle\}] = E[\{|\chi_i\rangle\}] + \sum_{ij} \epsilon_{ij}(\delta_{ij} - \langle\chi_i|\chi_j\rangle) \ . \tag{2.11}$$

Solving this variational problem in the basis which diagonalizes $\boldsymbol{\epsilon} = (\epsilon_{ij})_{i,j=1,\ldots,n}$ leads to a set of integro-differential equations, one for each spin-orbital. These equations are called canonical HARTREE-FOCK equations:

$$\hat{f}|\chi_i\rangle = \epsilon_i|\chi_i\rangle \tag{2.12}$$

with

$$\hat{f} = \hat{h} + \frac{1}{2}\sum_{j=1}^{N}\left(\hat{J}_j - \hat{K}_j\right) \tag{2.13}$$

and

$$\hat{h} = -\frac{1}{2}\sum_i \Delta_i - \sum_{iI}\frac{Z_i}{r_{iI}}, \tag{2.14}$$

$$\hat{J}_j|\chi_i(1)\rangle = \langle\chi_j(2)|r_{12}^{-1}|\chi_j(2)\rangle|\chi_i(1)\rangle \ , \tag{2.15}$$

$$\hat{K}_j|\chi_i(1) = \langle\chi_j(2)|r_{12}^{-1}|\chi_i(2)\rangle|\chi_j(1)\rangle \ . \tag{2.16}$$

The operators $\hat{J}_j$ and $\hat{K}_j$ are called COULOMB and exchange operators, respectively. While the COULOMB operator models a sort of averaged electronic repulsion, the exchange operator has no classical analogue. However, when the indices i and j coincide the exchange operator cancels exactly the contribution of the COULOMB operator. This is, the interaction of an electron with itself is naturally cancelled. From the above equations 2.15 and 2.16 it becomes clear that the integro-differential equation for each spin orbital depends on all other spin orbitals. This requires the solution to be of an iterative type, since the equations depend on their own solutions. The iterative solution is often referred to as *self consistent field* (SCF) procedure, since a final solution has to be stationary with respect to an application of the FOCK operator $\hat{f}$.

Since an analytical solution of the HARTREE-FOCK equations is not feasible in most cases, the spatial part of spin orbitals are normally expanded as a linear combination of analytical basis functions $\{\varphi_m\}$, i.e.:

$$|\chi_i\rangle = |\omega_i\rangle \sum_m c_{mi}|\varphi_m\rangle \ . \tag{2.17}$$

Inserting this ansatz into eq. 2.12 and projection onto the basis functions yields

$$\sum_m c_{mi} \underbrace{\langle\varphi_n|\hat{f}|\varphi_m\rangle}_{=:\mathbf{F}_{nm}} = \epsilon_i \sum_m c_{mi} \underbrace{\langle\varphi_n|\varphi_m\rangle}_{=:\mathbf{S}_{nm}} \qquad \forall_{i,n}, \tag{2.18}$$

which can be cast into a generalized matrix eigenvalue problem:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon} \ . \tag{2.19}$$

This formulation of the problem is called the ROOTHAAN-HALL matrix formalism [65, 66]. The entries of the diagonal matrix $\boldsymbol{\epsilon}$ are the orbital energies and the corresponding columns of $\mathbf{C}$ contain the expansion coefficients of the spin orbitals.

2.2.1.3 Restricted Hartree-Fock

Inserting the definitions of the FOCK operator 2.13 and the scalar product[6] into the definition for the FOCK matrix elements given in equations 2.18 yields a rather cumbersome but instructive equation system:

$$\begin{aligned}\mathbf{F}_{nm} = &\int_{\mathbb{R}^3\times\mathbb{S}} \varphi_n^* \hat{h} \varphi_m \mathrm{d}\tau\mathrm{d}\omega \\ &+ \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{S}}\int_{\mathbb{R}^3\times\mathbb{S}} \varphi_n^*(1)\varphi_m^*(2)\frac{1}{r_{12}}\varphi_n(1)\varphi_m(2)\mathrm{d}\tau_1\mathrm{d}\omega_1\mathrm{d}\tau_2\mathrm{d}\omega_2 \\ &- \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{S}}\int_{\mathbb{R}^3\times\mathbb{S}} \varphi_n^*(1)\varphi_m^*(2)\frac{1}{r_{12}}\varphi_m(1)\varphi_n(2)\mathrm{d}\tau_1\mathrm{d}\omega_1\mathrm{d}\tau_2\mathrm{d}\omega_2 \ .\end{aligned} \tag{2.20}$$

Considering the closed shell case of pairs of spin orbitals sharing a common spatial part, i.e.

$$\chi_j(i) = \left\{ \begin{array}{cc} & \phi_j(i)\cdot\alpha(i) \\ \text{or} & \phi_j(i)\cdot\beta(i) \end{array} \right. , \tag{2.21}$$

eq. 2.20 splits up into four parts, each dealing with one of the four primitive spin combinations

$$(\omega_n, \omega_m) \in \{(\alpha,\alpha),(\alpha,\beta),(\beta,\alpha),(\beta,\beta)\} \tag{2.22}$$

[6] The scalar product in the one particle space is the standard scalar product on the LEBESGUE space $\mathcal{L}^2(\mathbb{R}^3 \times \mathbb{S} \to \mathbb{C})$ of square integrable complex valued functions.

in the orbitals χ_n and χ_m. The spin integration now yields a factor of two in the one particle part and factors of four and two in the coulomb and exchange operators, respectively. This leads to a modified version of eq. 2.13 with the summation restricted to spatial indices:

$$\hat{f} = 2\hat{h} + \sum_{j=1}^{N/2} \left(2\hat{J}_j - \hat{K}_j \right) . \tag{2.23}$$

2.2.2 Many-Body Expansion of the Wavefunction

It is usually possible to gain more than 99% of the electronic energy within the Hartree-Fock approximation. Unfortunately the energy differences observed in chemical reactions are in general substantially smaller than one percent of the total electronic energy. Therefore, it is necessary to augment the Hartree-Fock method with suitable so-called correlation methods. The idea of correlation methods is to expand the wavefunction into a basis of Slater determinants. Thus the term many body expansion refers to an expansion in a set of many electron functions.

The occupied and virtual orbitals of a Hartree-Fock calculation are a suitable start for the setup of a many particle basis. By successively substituting occupied orbitals in the ground state Slater determinant by virtual orbitals, a hierarchy of different many body functions can be obtained:

$$\mathcal{B}_{\mathrm{MB}} = \{\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}, \ldots\} . \tag{2.24}$$

2.2.2.1 Linear Expansion: Configuration Interaction

The most straightforward way of the expansion of the wavefunction in a many electron basis is the linear expansion. Given the many particle basis 2.24 the expansion can be written as

$$|\Psi_{\mathrm{CI}}\rangle = |\Phi_0\rangle + \sum_{ia} c_i^a |\Phi_i^a\rangle + \left(\frac{1}{2!}\right)^2 \sum_{ijab} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \ldots , \tag{2.25}$$

where the abbreviation CI stands for *configuration interaction*, which is the name of this ansatz. Usually the coefficients $c_{ij\ldots}^{ab\ldots}$ are determined via the solution of an eigenvalue problem (eq. 2.29) obtained by insertion of the wavefunction ansatz into the Schrödinger equation and projection onto the many body basis functions (eq. 2.27):

$$\hat{H}|\Psi_{\mathrm{CI}}\rangle = \tilde{E}(|\Psi_{\mathrm{CI}}\rangle + |\Psi_{\mathrm{error}}\rangle) \qquad |\langle\Psi_X| \quad \forall_X \tag{2.26}$$

$$\Rightarrow \langle\Psi_X|\hat{H}|\sum_Y c_Y \Phi_Y\rangle = \tilde{E}(\langle\Phi_X|\sum_Y c_Y \Phi_Y\rangle + \langle\Phi_X|\Psi_{\mathrm{error}}\rangle) . \tag{2.27}$$

Forcing the projection of the error wavefunction to be zero, one arrives at

$$\sum_Y c_Y \langle\Phi_X|\hat{H}|\Phi_Y\rangle = \tilde{E} \sum_Y c_Y \langle\Phi_X|\Phi_Y\rangle \qquad \forall_X , \tag{2.28}$$

which can finally be cast into a generalized matrix eigenvalue equation form:

$$\mathbf{H}\vec{c} = \tilde{E}\mathbf{S}\vec{c}, \tag{2.29}$$

where $\mathbf{H}_{XY} = \langle\Phi_X|\hat{H}|\Phi_Y\rangle$ and $\mathbf{S}_{XY} = \langle\Phi_X|\Phi_Y\rangle$. It should be noted that for orthonormal sets of spin orbitals the matrix $\mathbf{S}$ collapses to the identity matrix, simlifying the problem to a casual eigenvalue problem.

2.2.2.2 Full CI and Truncated CI Versions

The size of the occupied and virtual spaces obtained from the preceding independent particle method determine the size of the configuration interaction Hamiltonian and overlap matrices. The size of the many body basis set is given by:

$$\#\mathbb{B}_{\mathrm{MB}} = \binom{\#\mathbb{W}}{n}, \tag{2.30}$$

where n is the number of electrons. Even though the CI-matrices are normally sparse, it is clear from the factorially increasing size of $\mathbb{B}_{\mathrm{MB}}$ that only calculations for a small number of basis functions are feasible. Due to this the so-called *full* CI ansatz (meaning that $\hat{H}$ is represented in the full many particle basis set) was used only for high accuracy benchmark calculations on small systems up to now. It should be noted that very recently several frameworks have been developed that employ the statistical Monte-Carlo method in full CI calculations on larger systems with encouraging success (see e.g. [67]).

Nevertheless *truncated* CI methods are widely used for several decades now in quantum chemistry. These methods rely on a truncated version of equation 2.25, where, for example, only the up to doubly substituted part of the many particle basis set $\mathbb{B}_{\mathrm{MB,SD}} = \{\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}\}$ is used to represent the Hamiltonian. In the spirit of this truncation, a hierarchy of methods with increasing accuracy can be obtained (CI up to singles substitutions CIS[7], CI up to doubles substitutions CISD, CISDT, . . .).

Finally, it should be noted that even for truncated CI methods it is not common practice to solve the entire eigenvalue problem. Since the solution of the eigenvalue problem requires a matrix inversion (computationally scaling as N^3) or a similar process and normally only the lowest eigenvalue (i.e. the ground state energy) is sought, it is reasonable to employ numerical recipes that were developed for this task only, e.g. the Davidson algorithm [68], which scales as N^2.

[7] For a canonical closed shell or unrestricted Hartree-Fock reference determinant Brillouin's theorem states that there is no interaction between singly substituted determinants and the reference via the Hamiltonian. Thus CIS does not improve the independent particle model. It is therefore not used for ground state calculations.

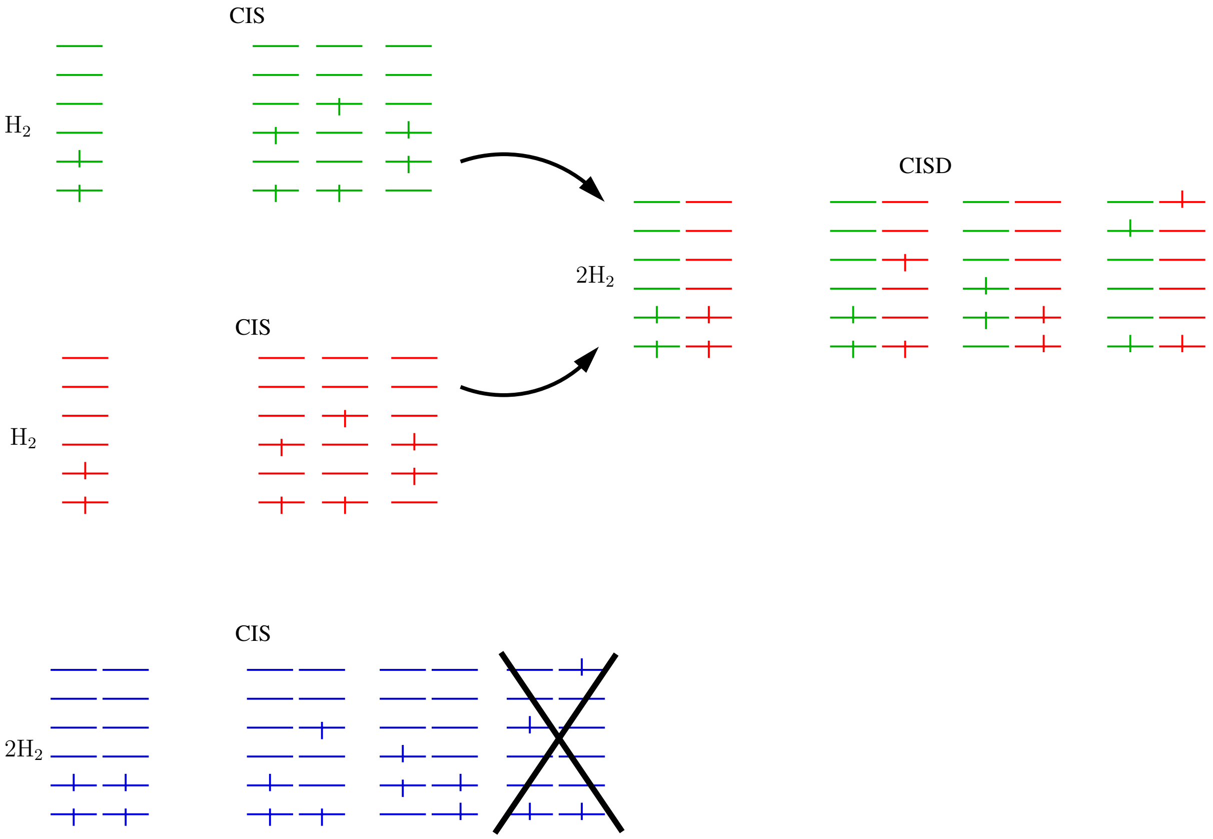


Figure 2.1: Scheme of a CIS calculation of a system of two independent hydrogen molecules in contrast to two separate CIS calculations of the individual fragments.

2.2.3 Size Consistency and the Product Expansion

The CI ansatz has several very important features such as an conceptually easy setup, variationallity[8] and several extensions to more general theories, dealing with excited states (CIS), non-single determinant references (*multi-reference* CI, MRCI) and also nuclear movement (*vibrational* CI, VCI). Despite this, it also has (in all of its variants excluding full CI) a severe drawback, namely its lack of size consistency and size extensivity.

Size consistency is a property that describes the qualitatively right dissociation into non-interacting systems (e.g. several molecules at infinite distances). For non-interacting systems it is trivially clear that the Hamiltonian should be a plain sum of the Hamiltonians of the individual subsystems. Thus, the total wavefunction has to be an antisymmetrized product of the individual wavefunctions and the energy should behave additively.

As can be seen in figure 2.1 the CIS method does not meet these requirements for a system of non-interacting hydrogen molecules. The product wavefunction of the individual CIS calculations contains doubly substituted determinants that do not show up in the CIS

[8] i.e. resulting from a variational ansatz, the CI energy is an upper bound for the exact energy of the system concidered.

calculation of the complete system. Obviously at least one of the drawbacks of the CI method is the lack of product substitutions in the wavefunction.

A possible workaround to this problem is to include product substitutions via a product expansion of the wavefunction as introduced in eq. 2.31:

$$|\Psi\rangle = \prod_i (1 + \hat{C}_i)|\Phi_0\rangle \,, \tag{2.31}$$

where the $\hat{C}_i$ operators transform the reference function into the substituted determinants included in the (truncated) many particle basis set. As the number of individual coefficients in the expansion does not increase with respect to the linear expansion, it is clear that for an increasing level of truncation the wavefunction converges to the full CI wavefunction.

Fortunately, this is not the only favorable feature of the product ansatz. It can be shown that the ansatz is size consistent as well as size extensive, a property introduced in the next chapter. For commuting and nilpotent substitution operators the product ansatz can alternatively be written as an operator exponential:

$$\prod_i (1 + \hat{C}_i)|\Phi_0\rangle = \exp\left(\sum_i \hat{C}_i\right)|\Phi_0\rangle \,. \tag{2.32}$$

This exponential ansatz is a characteristic of the *coupled cluster* method discussed in the next chapter.

2.2.4 Algebraic Properties of the Expansion Coefficients

The expansion coefficients occuring in the coupled cluster framework are normally called amplitudes. In order to distinguish them from the CI coefficients, the symbol t has been introduced for their representation, alongside the symbols $\hat{T}$ and $\hat{\tau}$ for the cluster and substitution operators, respectively.

Although it is possible to find algebraic relations between the quantities occuring in CI and coupled cluster, the newly introduced symbols represent more than just a cosmetic change. It can be shown that the sets of coefficients occuring in CI and CC equations have different statistical properties. Perhaps the most striking difference is their scaling behaviour with respect to the system size, leading to size extensive equations for the coupled cluster ansatz while the truncated configuration interaction method lacks this property. Furthermore in the coupled cluster framework, the amplitudes are size intensive, which leads to a linear scaling of the energy with the system size.

Chapter 3

Coupled Cluster Theory

Contents

3.1 Introduction

3.1.1 The Coupled Cluster Wavefunction

The basic idea of coupled cluster theory is the exponential ansatz for the wavefunction [1, 2]:

$$|\Psi_{\mathrm{CC}}\rangle = \exp(\hat{T})|\Phi_0\rangle \ . \tag{3.1}$$

Herein the reference wavefunction $|\Phi_0\rangle$ is the ground state Slater determinant obtained via a single particle method (in most cases $|\Phi_0\rangle$ corresponds to the Hartree-Fock wavefunction). The excitation operator $\hat{T}$ is defined as follows:

$$\begin{aligned} \hat{T} &= \sum_n \hat{T}_n &(3.2)\\ &= \sum_n t^{a_1 \dots a_n}_{i_1 \dots i_n} \, \hat{\tau}^{a_1 \dots a_n}_{i_1 \dots i_n} \; . &(3.3) \end{aligned}$$

The tensor entries t are the variables that have to be determined in an actual CC-calculation and the substitution operators

$$\hat{\tau}^{a_1 \dots a_n}_{i_1 \dots i_n} = \hat{a}^\dagger_{a_n} \dots \hat{a}^\dagger_{a_1} \hat{a}_{i_1} \dots \hat{a}_{i_n} \tag{3.4}$$

are defined via the second quantized [69, 48, 70] annihilation and creation operators, $\hat{a}_p$ and $\hat{a}^\dagger_q$, respectively.

It can be shown that the exponential ansatz 3.1 is equivalent to the product expansion mentioned in the previous chapter (cf. eq. 2.31), assuming special circumstances. Hence the drawback of size inconsistency is overcome by an exponential definition of the wavefunction and a suitable determination of the expansion coefficients.

3.1.2 The Projected Schrödinger Equation

The insertion of eq. 3.1 into the Schrödinger equation yields

$$\hat{H} e^{\hat{T}} |\Phi_0\rangle = \tilde{E} \left(e^{\hat{T}} |\Phi_0\rangle + |\Psi_{\text{error}}\rangle \right) \; . \tag{3.5}$$

From this equation an energy decoupled set of equations can be obtained by multiplication with $e^{-\hat{T}}$ from the left and projection upon the reference and excited determinants:

$$\begin{aligned} & \langle \Phi_X | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = \tilde{E} \left(\langle \Phi_X | e^{-\hat{T}} e^{\hat{T}} | \Phi_0 \rangle + |\Psi_{\text{error}}\rangle \right) &(3.6)\\ \Rightarrow \quad & \langle \Phi_X | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = \delta_{X0} \tilde{E} \, , &(3.7) \end{aligned}$$

where the orthonormality of the Slater-determinants was employed, the projection of the error was forced to be zero and non-overlapping sets of occupied and virtual orbitals were assumed.

The projection upon the reference determinant ($X = 0$ in eq. 3.7) is called the energy equation, since it is the only equation the energy is still contained in. The remaining equations are called amplitude equations, since they are employed for the determination of the expansion coefficients (amplitudes) occuring in the equations. It is noteworthy that the solution of this equation system does not correspond to the solution of an eigenvalue problem anymore, and that it is not variational anymore. In fact, the amplitude equations form a system of non linear equations that is normally solved by fixpoint iteration procedure. After convergence, the coefficients of the excitation operators in $\hat{T}$ can inserted into the energy equation to obtain the solution for the energy.

3.1.3 Size Extensivity

In addition to the feature of size consistency introduced in the last chapter there is also a concept of size extensivity. While size consistency ensures the right scaling of the correlation energy with the system size of non-interacting fragments, size extensivity deals with interacting systems.

From a phenomenological point of view it is clear that the correlation energy should scale proportionally to the system size (i.e. should be an extensive property). The definition of the extensivity is the following:

$$\lim_{N\to\infty} \frac{E_{\text{corr}}(N\cdot A)}{N} = \text{const}\,, \tag{3.8}$$

where a system of interacting and equal subsystems A is considered.

It is noteworthy that e.g. the CID approach fails to reproduce this scaling, but rather scales as $\sqrt{N}$ in the limit of large system sizes (see [54] p. 14f).

3.2 Algebraic Framework

3.2.1 The Concept of Normal Order

The definition of second quantized annihilation and creation operators reveals the effect of their action upon the real vacuum state $|\,\rangle$:

$$\hat{a}_x|\,\rangle = \langle\,|\hat{a}_x^\dagger = 0, \qquad x \in \{i, j, \ldots, a, b, \ldots\}\,. \tag{3.9}$$

Upon introduction of the ground state Slater determinant as a reference vacuum state (also called Fermi-vacuum) $|\Phi_0\rangle = |i_1 \ldots i_n\rangle$, the following somehow similar relations can be obtained:

$$\hat{a}_{a_k}|\Phi_0\rangle = \langle\Phi_0|\hat{a}_{a_k}^\dagger = 0, \quad a_k \in \mathbb{V} \tag{3.10}$$

$$\text{and}\;\; \hat{a}_{i_k}^\dagger|\Phi_0\rangle = \langle\Phi_0|\hat{a}_{i_k} = 0, \quad i_k \in \mathbb{O}\,. \tag{3.11}$$

It is clear from the inspection of eq. 3.9 that any expectation value of a string of second quantized operators regarding the true vacuum must vanish, if all creation operators are placed to the left of all annihilation operators. Such a string of operators is called *normal ordered.*

From the basic anti-commutation relations

$$[\hat{a}_p, \hat{a}_q]_+ = [\hat{a}_p^\dagger, \hat{a}_q^\dagger]_+ = 0 \tag{3.12}$$

$$\text{and}\;\; [\hat{a}_p, \hat{a}_q^\dagger]_+ = [\hat{a}_p^\dagger, \hat{a}_q]_+ = \delta_{pq}\,. \tag{3.13}$$

of second quantized operators a normal ordered pair of operators can be obtained by the following transformation (the asterisk replaces the dagger and non-dagger variants of the operators):

$$\{\hat{a}_p^*\hat{a}_q^*\}_N = [\hat{a}_p^*, \hat{a}_q^*]_+ - \hat{a}_p^*\hat{a}_q^*\,, \tag{3.14}$$

where $\{\,\}_N$ is the normal ordered operator string and $[\,,\,]_+$ is the anti-commutator. The expectation value of any pair of operators is then given by

$$\langle\,|\hat{a}_p^* \hat{a}_q^*|\,\rangle = \langle\,|[\hat{a}_p^*, \hat{a}_q^*]_+|\,\rangle - \langle\,|\{\hat{a}_p^* \hat{a}_q^*\}_N|\,\rangle \tag{3.15}$$

$$= \langle\,|[\hat{a}_p^*, \hat{a}_q^*]_+|\,\rangle\ . \tag{3.16}$$

This type of operation is called a contraction because the anti-commutation relations for operator pairs yield scalar values. Thus in summary the rules for the contraction operation (symbolized by a staple shaped line " $\sqcap$ " joining the two operators) can be written as follows:

$$\wick{\c{\hat{a}}_p^* \c{\hat{a}}_q^*} = \hat{a}_p^* \hat{a}_q^* - \{\hat{a}_p^* \hat{a}_q^*\}_N\ . \tag{3.17}$$

In other words, any pair of operators can be written as the sum of the normal ordered string and its contraction (which is obviously normal ordered):

$$\hat{a}_p^* \hat{a}_q^* = \{\hat{a}_p^* \hat{a}_q^*\}_N + \{\wick{\c{\hat{a}}_p^* \c{\hat{a}}_q^*}\}_N\ . \tag{3.18}$$

An expression for operator strings of arbitrary length known as Wick's theorem [71] can be derived in an inductive way (see e.g. [54], p. 70f for a sketch of the proof):

$$\begin{aligned} ABC\dots XYZ = \{ABC\dots XYZ\}_N &+ \sum_{\text{SINGLES}} \{\wick{\c A \c B C\dots XYZ}\}_N \\ &+ \sum_{\text{DOUBLES}} \{\wick{\c1 A \c2 B \c1 C\dots XY \c2 Z}\}_N \\ &+ \dots\ . \end{aligned} \tag{3.19}$$

3.2.1.1 Particle-Hole Formalism

From the inspection of the reference determinant

$$|\Phi_0\rangle = \prod_{i\in\mathbb{O}} \hat{a}_i^\dagger|\,\rangle\,, \tag{3.20}$$

it is clear that all creation operators occuring in its definition have to be shifted to the left of any annihilation operator applied to the reference. Both the application of the anticommutation rules 3.12, 3.13 and the application of Wick's theorem would be very clumsy in this framework. In particular, the effort to be taken to convert an expression to its normal ordered form would be dependent on the number of electrons present in the system considered.

For the reasons mentioned above it is convenient to re-define the concept of normal order. To achieve a particle number independent framework, it is required for a normal ordered string of operators that all creation operators of occupied orbitals (*holes*) are placed on the right hand side of all hole annihilators and that all creators of virtual orbitals (*particles*) are placed on the left hand side of all particle annihilators. Due to this definition every particle number conserving normal ordered string of operators acting on the reference determinant will yield a zero result, since the right most operator either destroys a virtual orbital or creates an occupied one (see eqs. 3.10 and 3.11).

However, the re-definition of normal ordering has a drawback. Since now the normal ordering depends on the nature of the orbital indices, the contraction process also shows this dependency. One can derive the contraction rules for normal ordered (with respect to the Fermi vacuum) operator strings to be:

$$\{\overbrace{\hat{a}^\dagger_p\hat{a}_q}\} = \delta_{pq\in\mathbb{O}} \tag{3.21}$$

$$\text{and} \qquad \{\overbrace{\hat{a}_p\hat{a}^\dagger_q}\} = \delta_{pq\in\mathbb{V}} \ . \tag{3.22}$$

$$\tag{3.23}$$

Contractions between creators only and annihilators only vanish, because these strings are normal ordered already.

Thus, the price to pay for the particle independence of the contraction process is the necessity to distinguish between contractions in the occupied and virtual spaces, respectively. Nevertheless, for a convenient and universal framework, this drawback is of minor importance. In the following the term normal order will always refer to the re-definition given in this section.

3.2.1.2 The Normal Ordered Hamiltonian

According to the rules of the second quantization framework the electronic Hamiltonian (cf. eq. 2.2) can be written as

$$^{\mathrm{sq}}\hat{H}_{\mathrm{el.}} = \sum_{pq} h^q_p \hat{a}^\dagger_q \hat{a}_p + \frac{1}{2}\sum_{prqs} v^{qs}_{pr}\hat{a}^\dagger_s\hat{a}^\dagger_q\hat{a}_p\hat{a}_r \ , \tag{3.24}$$

wherein $h^q_p = \langle q|\hat{h}|p\rangle$ is the matrix element of the one particle part of the Hamiltonian (i.e. the kinetic energy term of the electrons and the electron nuclei interaction term) and $v^{qs}_{pr} = \langle qs|\hat{v}|pr\rangle$ is the matrix element of the electron-electron interaction (i.e. $\hat{v} = r^{-1}_{12}$). The factor of one half in front of the two particle part of 3.24 is due to particle symmetry in $\hat{v}$ and ensures that every interaction is counted once only.

For the sake of convenience the one particle and two particle parts of the Hamiltonian will be recast into their normal ordered form individually. This will be done via Wick's theorem eq. 3.19.

Two particle part It is convenient to discuss the two particle part in the beginning, since its normal ordering reveals effective one particle operators which can be included into the ordering process of the one particle operator. The normal ordered form of the two particle part of the Hamiltonian according to WICK's theorem contains up to doubly contracted terms:

$$\begin{aligned}\hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r = \ & \{\hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r\}_N + \wick{\{\c{\hat{a}}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \c{\hat{a}}_r\}_N} + \wick{\{\hat{a}_s^\dagger \c{\hat{a}}_q^\dagger \hat{a}_p \c{\hat{a}}_r\}_N} + \wick{\{\c{\hat{a}}_s^\dagger \hat{a}_q^\dagger \c{\hat{a}}_p \hat{a}_r\}_N} \\ & + \wick{\{\hat{a}_s^\dagger \c{\hat{a}}_q^\dagger \c{\hat{a}}_p \hat{a}_r\}_N} + \wick{\{\c1{\hat{a}}_s^\dagger \c2{\hat{a}}_q^\dagger \c2{\hat{a}}_p \c1{\hat{a}}_r\}_N} + \wick{\{\c1{\hat{a}}_s^\dagger \c2{\hat{a}}_q^\dagger \c1{\hat{a}}_p \c2{\hat{a}}_r\}_N} \,, \qquad (3.25)\end{aligned}$$

which can be evaluated by application of the antisymmetry of the normal ordering and by contraction:

$$\begin{aligned}\hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r = \ & \{\hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r\}_N + \delta_{rs\in\mathbb{O}}\{\hat{a}_q^\dagger \hat{a}_p\}_N - \delta_{rq\in\mathbb{O}}\{\hat{a}_s^\dagger \hat{a}_p\}_N - \delta_{ps\in\mathbb{O}}\{\hat{a}_q^\dagger \hat{a}_r\}_N \\ & + \delta_{pq\in\mathbb{O}}\{\hat{a}_s^\dagger \hat{a}_r\}_N + \delta_{rs\in\mathbb{O}}\delta_{pq\in\mathbb{O}} - \delta_{rq\in\mathbb{O}}\delta_{ps\in\mathbb{O}} \ . \qquad (3.26)\end{aligned}$$

Due to the arbitrary choice of summation indices the second and fifth and the third and fourth terms coincide, respectively:

$$\begin{aligned}\hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r = \ & \{\hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r\}_N + 2\delta_{rs\in\mathbb{O}}\{\hat{a}_q^\dagger \hat{a}_p\}_N - 2\delta_{rq\in\mathbb{O}}\{\hat{a}_s^\dagger \hat{a}_p\}_N \\ & + \delta_{rs\in\mathbb{O}}\delta_{pq\in\mathbb{O}} - \delta_{rq\in\mathbb{O}}\delta_{ps\in\mathbb{O}} \ . \qquad (3.27)\end{aligned}$$

The two particle part can now be written in the following way:

$$\begin{aligned}\frac{1}{2}\sum_{prqs} v_{pr}^{qs} \hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r = & \frac{1}{2}\sum_{prqs} v_{pr}^{qs} \{\hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p \hat{a}_r\}_N + \sum_{ipq} (v_{pi}^{qi} - v_{pi}^{iq})\{\hat{a}_q^\dagger \hat{a}_p\}_N \\ & + \frac{1}{2}\sum_{ij}\left(v_{ij}^{ij} - v_{ij}^{ji}\right) \ . \qquad (3.28)\end{aligned}$$

The contractions reveal a one particle and a scalar part in the two particle part of the Hamiltonian. It is convenient to discuss the one particle part together with the original one particle part of the Hamiltonian. This requires a substitution:

$$h_p^q \to h_p^q + \sum_i (v_{pi}^{qi} - v_{pi}^{iq}) =: f_p^q \ . \qquad (3.29)$$

One Particle Part The application of WICK's theorem to the one particle part of the Hamiltonian yields

$$\sum_{pq} f_p^q \hat{a}_q^\dagger \hat{a}_p = \sum_{pq} f_p^q \{\hat{a}_q^\dagger \hat{a}_p\}_N + \sum_{pq} f_p^q \wick{\{\c{\hat{a}}_q^\dagger \c{\hat{a}}_p\}_N} \qquad (3.30)$$

$$= \sum_{pq} f_p^q \{\hat{a}_q^\dagger \hat{a}_p\}_N + \sum_{pq} f_p^q \delta_{pq\in\mathbb{O}} \ . \qquad (3.31)$$

Thus it is possible to separate the one particle part into a fully normal ordered and a fully contracted (meaning scalar) part:

$$\hat{f} = \hat{f}_N + \sum_i f_i^i \ . \qquad (3.32)$$

3.2.2 The Baker-Campbell-Hausdorff Expansion

After the procedure of normal ordering of the second quantized Hamiltonian the projected coupled cluster equations can be rewritten in terms of normal ordered and scalar parts of the Hamiltonian:

$$\langle\Phi_X|e^{-\hat{T}}(\hat{H}_N+E_{\mathrm{HF}})e^{\hat{T}}|\Phi_0\rangle=\delta_{0X}E \tag{3.33}$$

$$\Rightarrow\langle\Phi_X|e^{-\hat{T}}\hat{H}_N e^{\hat{T}}|\Phi_0\rangle=\delta_{0X}\underbrace{(E-E_{\mathrm{HF}})}_{=E_{\mathrm{corr}}}\ . \tag{3.34}$$

The quantity $E_{\mathrm{corr}}=E-E_{\mathrm{HF}}$ is the correlation energy in Löwdin's sense. The similarity transformed normal ordered Hamiltonian will be further investigated in the following.

A well known relation for operators which obey certain commutator relations (see section 4.3) is the so called Baker-Campbell-Hausdorff formula [72, 73, 74] (also known as Hadamard's lemma) 3.35 which expands a similarity transformed operator into a series of nested commutators:

$$e^{-\hat{B}}\hat{A}e^{\hat{B}}=\sum_{i=0}^{\infty}\frac{1}{i!}\underbrace{[\ldots[}_{i\text{ times}}\hat{A}\underbrace{,\hat{B}]\ldots,\hat{B}]}_{i\text{ times}}\ . \tag{3.35}$$

This in principle infinite series has the property to truncate naturally for the coupled cluster equations. This is due to the maximal rank of the Hamiltonian which determines the maximal number of substitution operators that can be connected to it. Since the two-particle part of the normal ordered Hamiltonian contains four operators, the Hamiltonian can be connected to at most four substitution operators. The expansion of the similarity transformed Hamiltonian thus takes the following form:

$$\begin{aligned}e^{-\hat{T}}\hat{H}_N e^{\hat{T}}=&\ \hat{H}_N+[\hat{H}_N,\hat{T}]+\frac{1}{2}[[\hat{H}_N,\hat{T}],\hat{T}]\\&+\frac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}]+\frac{1}{24}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]\ .\end{aligned} \tag{3.36}$$

The last step in the term simplification consists of the evaluation of the terms in the nested commutator expansion and projections thereof via Wick's theorem for normal ordered operator products, eq. 3.37:

$$\begin{aligned}\{ABC\ldots\}_N\{XYZ\ldots\}_N=&\ \{ABC\ldots XYZ\ldots\}_N\\&+\sum_{\text{SINGLES}}\{\overline{ABC\ldots X}YZ\ldots\}_N\\&+\sum_{\text{DOUBLES}}\{\overline{A\overline{BC\ldots X}Y}Z\ldots\}_N\\&+\ldots\ .\end{aligned} \tag{3.37}$$

Please note that contractions of operators which belong to the same initial product do not occur. It is also noteworthy that due to the FERMI vacuum expectation value only fully contracted terms can contribute to the coupled cluster equations.

For reasons of clarity a short example of the term simplification will be given. A singles projection term of the FOCK operator will be chosen. A left arrow will indicate a "contributes to" relation:

$$\langle \Phi_I^A | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle \quad \longleftarrow \quad \frac{1}{4}\, \hat{a}_I^\dagger \hat{a}_A [\hat{F}_N, \hat{T}_2] \; . \tag{3.38}$$

A single term of this commutator can be written as:

$$\hat{a}_I^\dagger \hat{a}_A [\hat{F}_N, \hat{T}_1] \quad \longleftarrow \quad \sum_{pqia} f_p^q t_i^a \hat{a}_I^\dagger \hat{a}_A \{\hat{a}_q^\dagger \hat{a}_p\}_N \hat{a}_a^\dagger \hat{a}_i \tag{3.39}$$

$$\longleftarrow \quad \sum_{pqia} f_p^q t_i^a \{\hat{a}_I^\dagger \hat{a}_A\}_N \{\hat{a}_q^\dagger \hat{a}_p\}_N \{\hat{a}_a^\dagger \hat{a}_i\}_N \; . \tag{3.40}$$

In the last transformation it was employed that excitation operators as well as de-excitation operators are already normal ordered. Now one fully contracted term of WICK's theorem 3.37 will be chosen:

$$\{\hat{a}_I^\dagger \hat{a}_A\}_N \{\hat{a}_q^\dagger \hat{a}_p\}_N \{\hat{a}_a^\dagger \hat{a}_i\}_N \quad \longleftarrow \quad \{\overbrace{\hat{a}_I^\dagger \overbrace{\hat{a}_A \hat{a}_q^\dagger} \overbrace{\hat{a}_p \hat{a}_a^\dagger} \hat{a}_i}\}_N \tag{3.41}$$

$$\longleftarrow \quad \delta_{Ii} \delta_{Aq} \delta_{pa} \; . \tag{3.42}$$

The KRONECKER symbols indicate that the indices I,A and p are contracted with i,q and a, respectively. Due to that the summation over p and q vanishes and one term of the singles projection can be broken down to yield

$$\langle \Phi_I^A | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle \quad \longleftarrow \quad \sum_{ia} f_a^A t_I^a \; . \tag{3.43}$$

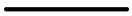
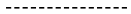
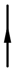
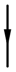
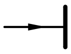
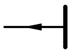
3.3 Diagrammatic Approach to Coupled Cluster Theory

Since their introduction the GOLDSTONE diagrams [75, 76, 77, 78, 79] have played an important role in many body theory. The basic idea behind these diagrams is to represent messy formulae in a more striking and human readable form.

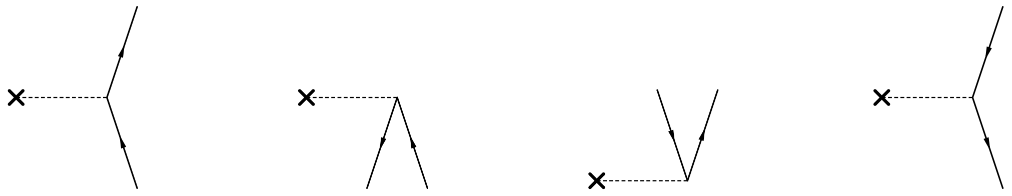
3.3.1 Definitions

Coupled cluster diagrams basically consist of the fragments shown in table 3.1. For example the one particle part of the Hamiltonian consists of four diagrams each of which depicts one of the possible index combinations (i,j), (i,a), (a,i) or (a,b). The corresponding diagrams are augmented by a cross that represents the $\hat{f}$-operator (see fig. 3.1).

Table 3.1: Fragments occurring in coupled cluster Goldstone diagrams.

Diagram fragment	Fragment name	Functionality
	Cluster line	Depicts a cluster operator $\hat{T}$
	Interaction line	Depicts a part of the Hamiltonian
	Particle line	Depicts a particle (virtual orbital)
	Hole line	Depicts a hole (occupied orbital)
	Incoming line	Depicts an annihilator
	Outgoing line	Depicts a creator

Once the elementary diagram components are defined the Wick contractions of operator strings can easily be depicted by joining the lines that represent the contracted indices (as shown in fig 3.2).

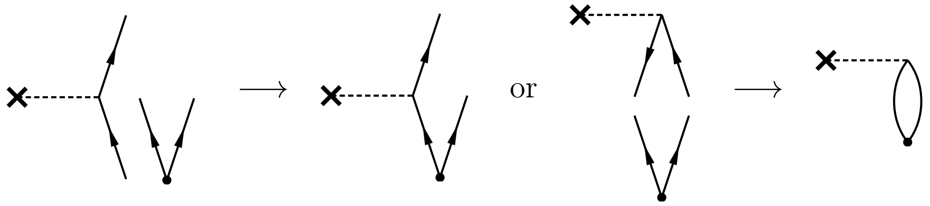


$\sum_{ab} f_a^b\{\hat{a}_b^\dagger \hat{a}_a\}_N$ $\sum_{ia} f_a^i\{\hat{a}_i^\dagger \hat{a}_a\}_N$ $\sum_{ia} f_i^a\{\hat{a}_a^\dagger \hat{a}_i\}_N$ $\sum_{ij} f_i^j\{\hat{a}_j^\dagger \hat{a}_a\}_i$

Figure 3.1: Picture of the diagrams contributing to the Fock operator.

For reasons of beauty and a fast detection of the scaling behaviour, a double contraction of indices that originate at the same vertex on both operators is depicted as a loop. The loop on the right hand side of figure 3.2 originates in the contraction of both of the indices of the Fock operator with both indices of the $\hat{T}_1$ operator. Please note that upon contraction of the indices one summation on the left hand side and two summations on the right hand side collapse.

The Fermi vacuum expectation value ensures that only fully contracted terms can contribute to the coupled cluster equations. It is thus obvious that the term on the right hand side of figure 3.2 can contribute to the coupled cluster energy equation while the term on the left hand side has to be contracted to another pair of second quantized operators to yield a non vanishing term after the application of the Fermi vacuum expectation value.



$$\sum_{iabc} f_a^b t_i^c \{\hat{a}_b^\dagger \overbrace{\hat{a}_a \hat{a}_c^\dagger} \hat{a}_i\}_N \longrightarrow \sum_{iab} f_a^b t_i^a \{\hat{a}_b^\dagger \hat{a}_i\} \text{ or } \sum_{ijab} f_a^i t_j^b \{\overbrace{\hat{a}_i^\dagger \overbrace{\hat{a}_a \hat{a}_b^\dagger} \hat{a}_j}\}_N \longrightarrow \sum_{ia} f_a^i t_i^a$$

Figure 3.2: Two possible contractions of the Fock operator with a single substitution operator.

3.3.2 Precontracted Diagrams

One corollary of the non existing contractions within a single product in Wick's second theorem is that precontracted diagrams (i.e. diagrams connecting indices associated to one single operator) do not occur. However, this is not the total truth. It is only due to the preceding normal ordering of the two particle part of the Hamiltonian that those diagrams do not explicitly show up. The normal ordering step produces precontracted diagrams that are afterwards assigned to the one particle part of the Hamiltonian and the reference energy. It is this step that reveals a part of the power of the concept of normal order. A large number of precontracted diagrams (and thus many algebraic terms) are excluded from the discussion of the coupled cluster equations by normal ordering and subsequent gathering of similar terms. The contributions of the two particle part to the Fock operator in terms of precontracted diagrams are shown in figure 3.3.

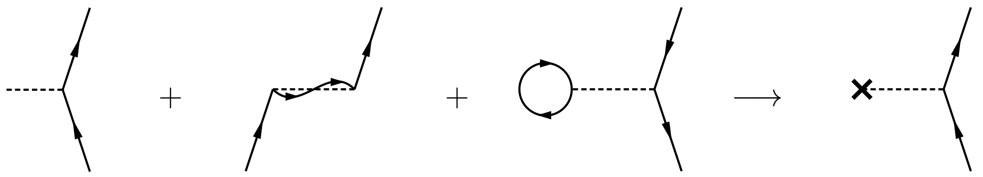
3.3.3 Generation of the Coupled Cluster Equations Employing Diagrams

Up to now the discussion of diagrams has been rather basic. There are of course certain rules for forward and backward translation of algebraic equations and Goldstone diagrams. For a detailed discussion of the derivation and application of the translation rules, see e.g. [54]. The rules and transformations will be investigated employing an example doubles substitution term in the following:

$$\langle \Phi_{IJ}^{AB} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle \quad \leftarrow \quad \sum_{ijab} v_{ij}^{ab} t_i^a t_j^A t_{IJ}^{Bb} \,. \tag{3.44}$$

The rules for the generation of diagrams are summarized below:

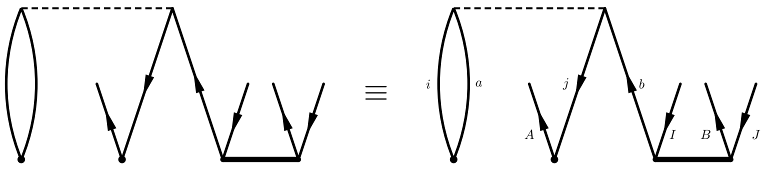
1. Construction of the lines representing the operators involved in the term, e.g. a cluster line for $\hat{T}_2$ or an interaction line for $\hat{V}$,



$$\sum_{pq} h_p^q \{\hat{a}_q^\dagger \hat{a}_p\}_N + \sum_{ipq} v_{ip}^{qi} \{\hat{a}_q^\dagger \hat{a}_p\}_N + \sum_{ipq} v_{ip}^{iq} \{\hat{a}_q^\dagger \hat{a}_p\}_N \longrightarrow \sum_{pq} f_p^q \{\hat{a}_q^\dagger \hat{a}_p\}_N$$

Figure 3.3: Scheme of the two-particle contributions to the Fock operator in diagrammatic notation. Please note that these diagrams are only representatives, since the uncontracted edges are not yet defined to be particles or holes.

2. Assignment of hole and/or particle lines to the vertices of the cluster/interaction lines according to the space the individual indices belong to,
3. Joining the hole/particle lines with common indices,
4. Transformation of double contractions of indices on the same vertices to loops,
5. Final cleanup.



$$\sum_{ijab} v_{ij}^{ab} t_i^a t_j^A t_{IJ}^{Bb}$$

Figure 3.4: Example of a doubles projection diagram of the two particle part of the normal ordered Hamiltonian.

The rules for the back transformation from diagrams to algebraic terms are more elaborate. One has to account for the pre-factors and signs of the terms from the topology of the connection of vertices. In the following a scheme for the back transformation will be given:

1. Assignment of tensor variable names to the cluster/interaction lines,
2. Assignment of index names to the particular connections according to the space the individual particle/hole line belongs to,
3. Distribution of the index names to the tensor symbols,
4. Generation of a pre-factor a via $a = 2^{(\#\text{equiv vertices}+\#\text{equiv internal lines})}$,
5. Generation of a sign s via $s = (-1)^{(\#\text{holes}-\#\text{loops})}$.
6. Summation over contracted indices.

3.4 Spin Independent Coupled Cluster in the Literature

The idea of a spin independent version of the working equations came up immediately at the beginning of coupled cluster theory in quantum chemistry. In several publications, ČÍŽEK and PALDUS [3, 4, 5] derived the working equations of spin free as well as spin orbital based coupled cluster doubles (originally called CPMET: *Coupled pair many electron theory*).

They did so by means of skeletons, predecessors of the nowadays very common coupled cluster diagrams. ČÍŽEK claims that the spin free variant of the working equations can be derived by omitting the maximum loop rule and application of a weighting factor of two for every loop occuring in the diagrams. However, it is not fully clear from his publication if he restricts himself to the CCD approximation or states a general rule.

For the relatively simple case of coupled cluster doubles his rule of thumb, nevertheless, can easily be understood by applying spin integration to the spin orbital terms.

3.4.1 Diagrammatic Approaches

The first reported implementation of a spin free coupled cluster routine including single and double substitutions is probably the one of BARTLETT ET AL. [9]. In their publication the authors derive working equations via GOLDSTONE diagrams.

The diagrammatic idea was probably exploited most in the work of PALDUS [80, 81, 82, 83]. He proposed many variants of coupled cluster type methods for different spin multiplicities and spin states via the combination of spatial diagrams (called skeletons) and spin diagrams. For example the skeleton of the double excitation $\hat{T}_2$ has to be combined with three spin diagrams representing the three possibilities to generate a spin conserving excitation (in the spin orbital case). Of course this yields far more fully contracted terms in the working equations due to the higher flexibility in the combination of the spin diagrams.

The idea of skeletons and spin diagrams was also exploited for the derivation of CCSD and CCSDT equations [13, 84, 85, 86] and extended very recently by Matthews, Stanton and Gauss [46] to derive CCSDT and CCSDTQ working equations in a spin free framework. They also report the implementation of the spin independent equations [47] in the CFOUR [87] program package.

3.4.2 Algebraic Approaches

For the, in contrast to higher substituted versions, relatively simple CCSD approximation many implementations exist up to now. Nearly every common quantum chemistry program package, including GAUSSIAN [88], TURBOMOLE [12], MOLPRO [10], MOLCAS [11] and many others, has a CCSD (and often also the perturbatively extended CCSD(T)) module. However, the up to date fastest implementation of a spin free version of CCSD is probably the one contained in MOLPRO suggested and implemented by Werner and coworkers [89]. It features a matrix based storage of the integral, amplitude, intermediate and residual tensors, respectively. This, despite having an unfavorable sparse storage of the tensor quantities, leads to a very efficient contraction algorithm.

The actual derivation of the working equations was most likely done via the evaluation of Wick's theorem for spin independent substitution operator strings. While this can easily be done for CCSD, the factorial increase of fully contracted terms limits the direct evaluation of Wick's theorem to low orders of substitution (i.e. CCSDTQ equations take about a day on a modern desktop computer to be derived). It is also noteworthy that in addition to its unfavorable scaling with the number of second quantized operators in an operator string the simplification of the CC equations via Wick's theorem in the spin free case bears another complexity. Due to the definition of the spin independent substitution operators as a sum of a pure α-spin term and a pure β-spin term, the number of operator strings to be evaluated after expansion of the products increases by a number of two for each single substitution operator involved. This combination of a factorial and an exponential scaling behavior truly restricts the application of Wick's theorem to very small examples. As an example the term

$$R_{IJ}^{AB} \longleftarrow \langle \Phi_{IJ}^{AB} | [[[\hat{V}_N, \hat{T}_2], \hat{T}_1], \hat{T}_1] | \Phi_0 \rangle \tag{3.45}$$

will be discussed. In the simplified CCSD equations the contribution of this term restricts itself to ten (four, if implicitely antisymmetrized) tensor products, although the evaluation via Wicks theorem includes a maximum of 752 terms. For the spin independent case this number of terms has to be multiplied by 2^8 yielding almost 200000 terms.

There are two further points to consider when talking about the working equations. First of all, due to the fact that Wick's theorem only accounts for operator strings and does not employ possible symmetries on the tensor quantities associated, the indices of arising terms have to be brought into a canonical order and the equations re-simplified to achieve a compact notation in the equation system. As a second point one has to consider a (partial) factorization of the equations to yield an optimal scaling (e.g. N^6

vs. N^8 for factorized in contrast to unfactorized CCSD working equations). Due to these complications the working equations are hard coded in many quantum chemistry packages. This circumvents the bottleneck of re-deriving and factoring out the equations for every run of the module.

Chapter 4

An Alternative Algebraic Framework

Contents

4.1 Definitions and Notational Remarks

For reasons of clarity, in the following, spin orbital indices will be denoted with under- and overbars for α and β spin functions, respectively. The same convention will be applied to the one particle spaces. If the nature of the spin function is not distinguished in the formula, spin orbitals will be identified with a tilde. So the following conventions hold:

$$\underline{i}, \underline{j}, \dots \in \underline{\mathbb{O}}, \qquad \underline{a}, \underline{b}, \dots \in \underline{\mathbb{V}}, \qquad \underline{p}, \underline{q}, \dots \in \underline{\mathbb{W}} \tag{4.1}$$

$$\overline{i}, \overline{j}, \dots \in \overline{\mathbb{O}}, \qquad \overline{a}, \overline{b}, \dots \in \overline{\mathbb{V}}, \qquad \overline{p}, \overline{q}, \dots \in \overline{\mathbb{W}} \tag{4.2}$$

$$\tilde{i}, \tilde{j}, \dots \in \tilde{\mathbb{O}}, \qquad \tilde{a}, \tilde{b}, \dots \in \tilde{\mathbb{V}}, \qquad \tilde{p}, \tilde{q}, \dots \in \tilde{\mathbb{W}} \tag{4.3}$$

The description of the coupled cluster method is based on the application of substitution operators $\hat{\tau}_{\tilde{p}}^{\tilde{q}}$ or $\hat{\eta}_{p}^{q}$ on a single determinant reference wavefunction. These operators can be depicted as (scaled) projection operators as follows:

$$\hat{\tau}_{\tilde{p}}^{\tilde{q}} = \sum_{i=1}^{n} |\chi_{\tilde{q}}(i)\rangle\langle\chi_{\tilde{p}}(i)| t_{\tilde{p}}^{\tilde{q}} \tag{4.4}$$

$$\text{and } \hat{\eta}_{p}^{q} = \sum_{i=1}^{n} |\phi_{q}(i)\rangle\langle\phi_{p}(i)| s_{p}^{q}\,, \tag{4.5}$$

where the symbol χ represents spin orbitals while ϕ represents spatial orbitals. The sum over the electron indices ensures that the (spin-)orbital p is replaced by q in every product contained in the determinant. The compound operators occuring in the coupled cluster equations as exponents, are defined as:

$$\hat{T} = \sum_{i} t_i \hat{\tau}_i, \text{and} \qquad \hat{E} = \sum_{i} e_i \hat{\eta}_i\ . \tag{4.6}$$

The spatial orbital substitution operators $\hat{\eta}_p^q$ (often called unitary group generators in the literature) can be expressed as the sum of two spin-orbital substitution operators:

$$\hat{\eta}_{p}^{q} = \hat{\tau}_{\underline{p}}^{\underline{q}} + \hat{\tau}_{\overline{p}}^{\overline{q}}\ . \tag{4.7}$$

To make use of the concept of second quantization, equation 4.7 can be employed to express the spatial orbital substitution operators in terms of annihilators and creators:

$$\hat{\eta}_{p}^{q} = \hat{a}_{\underline{q}}^{\dagger}\hat{a}_{\underline{p}} + \hat{a}_{\overline{q}}^{\dagger}\hat{a}_{\overline{p}}\ . \tag{4.8}$$

It is possible to define a concept of normal order also for the spatial orbital substitution operators. A string of these substitution operators will be called normal ordered if all addends in its expansion into spin orbital annihilation and creation operators are normal ordered, e.g.:

$$\{\hat{\eta}_{p}^{q}, \hat{\eta}_{r}^{s}\} = \{\hat{a}_{\underline{q}}^{\dagger}\hat{a}_{\underline{p}}\hat{a}_{\underline{s}}^{\dagger}\hat{a}_{\underline{r}}\} + \{\hat{a}_{\underline{q}}^{\dagger}\hat{a}_{\underline{p}}\hat{a}_{\overline{s}}^{\dagger}\hat{a}_{\overline{r}}\} + \{\hat{a}_{\overline{q}}^{\dagger}\hat{a}_{\overline{p}}\hat{a}_{\underline{s}}^{\dagger}\hat{a}_{\underline{r}}\} + \{\hat{a}_{\overline{q}}^{\dagger}\hat{a}_{\overline{p}}\hat{a}_{\overline{q}}^{\dagger}\hat{a}_{\overline{p}}\} \tag{4.9}$$

Many of the formulae presented in this chapter, however, apply to spin orbital as well as spatial orbital substitution operators. In the following, in these equations the variable σ will be used for operators and θ for orbitals:

$$\hat{\sigma}_{p}^{q} \in \{\hat{\tau}_{\tilde{p}}^{\tilde{q}}, \hat{\eta}_{p}^{q}\}\ . \tag{4.10}$$

In a similar fashion to the definition of the single particle substitution operators higher order operators can be defined. A particular care has to be given to the possibility of coinciding indices, as these can lead to hidden single substitutions. A double substitution operator has thus to written as:

$$\hat{\sigma}_{pq}^{rs} = \sum_{k,l=1}^{n} |\theta_s(l)\rangle|\theta_r(k)\rangle\langle\theta_q(k)|\langle\theta_p(l)| - \sum_{k=1}^{n} |\theta_s(k)\rangle\langle\theta_p(k)| \tag{4.11}$$

$$= \hat{\sigma}_{p}^{r}\hat{\sigma}_{q}^{s} - \delta_{rq}\hat{\sigma}_{p}^{s}\ . \tag{4.12}$$

Subtraction of the permuted operator $\hat{\sigma}_{qp}^{sr}$ yields a commutator relation that will be exploited in the derivation of the term simplification:

$$[\hat{\sigma}_{p}^{r}, \hat{\sigma}_{q}^{s}] = \delta_{ps}\hat{\sigma}_{q}^{r} - \delta_{qr}\hat{\sigma}_{p}^{s}\ . \tag{4.13}$$

4.1.1 Remark on the Name Unitary Group Generators

The name *Unitary Group Generators* [90, 91] most likely emerged out of a misunderstanding. It refers to the application of the so called unitary group generators (in terms of infinitesimal generators of $\mathrm{U}(n)$, i.e. members of the Lie algebra $\mathfrak{u}(n)$) $\hat{\eta}_p^q = \hat{a}^\dagger_{\underline{a}}\hat{a}_{\underline{i}} + \hat{a}^\dagger_{\overline{a}}\hat{a}_{\overline{i}}$ to the reference determinant.

In fact, the operators mentioned are not members of $\mathfrak{u}(n)$ in general. The standard representation of the unitary Lie algebra is the embedding in the linear space of $n \times n$-matrices, where $\mathfrak{u}(n)$ forms the subspace of skew-hermitian matrices. However, the operators $\hat{\eta}_p^q$ are, by no means, skew-hermitian.

Since the exponential of a skew-hermitian matrix is unitary (as can easily be proven by explicit calculation) the transformation

$$\hat{H}' = e^{-\hat{E}}\hat{H}e^{\hat{E}}, \tag{4.14}$$

$$|\Psi\rangle = e^{\hat{E}}|\Phi_0\rangle \tag{4.15}$$

would not affect the norm of the wavefunction. This would imply that the coupled cluster wavefunction would be normalized (as it is in general known not to be).

Nevertheless, it is possible to construct the two skew-hermitian operators (cf. [92] eq. 4.2.8)

$$\hat{\eta}_+ = \frac{i}{\sqrt{2}}(\hat{\eta}_p^q + \hat{\eta}_q^p) \tag{4.16}$$

and

$$\hat{\eta}_- = \frac{1}{\sqrt{2}}(\hat{\eta}_p^q - \hat{\eta}_q^p) \tag{4.17}$$

as complex linear combinations [93]. However, these operators always combine excitations with de-excitations and vice versa, which leads to an infinite expansion when employing the BCH-Formula.

Discussions on truncated versions (i.e. correct to a given order of perturbation theory) of a unitary coupled cluster (UCC) theory employing scaled variants of the operators $\hat{\eta}_-$ from above were given by Bartlett et al. [94, 95].

4.2 Normal Ordering of Substitution Operators

Since pure excitation operators as well as pure de-excitations are in normal order with respect to the Fermi vacuum already, special attention has to be payed regarding the operators included in the hamiltonian. In the process described below, the spin independent second quantized operators will be employed. The results for the spin orbital operators are well known and also can be obtained by considering the all-α terms below only.

For the one particle part of the hamiltonian the substitution operator can be written as:

$$\hat{\eta}_p^q = \hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}} + \hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}} = \{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\} + \delta_{\underline{pq}\in\underline{\mathbb{O}}} + \{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\} + \delta_{\overline{pq}\in\overline{\mathbb{O}}} \, , \tag{4.18}$$

where WICKs theorem was employed. Replacing spin indices with spatial indices on the right hand side one obtains

$$\hat{\eta}_p^q = \{\hat{\eta}_p^q\} + 2\delta_{pq\in\mathbb{O}} \, . \tag{4.19}$$

Inserting this result in the complete expression for the one particle part yields:

$$\hat{h} = \sum_{pq} h_p^q\{\hat{\eta}_p^q\} + 2\sum_i h_i^i \, . \tag{4.20}$$

Please note that due to normal ordering, contractions between p and q are not allowed anymore.

The expression for the two particle operator reads

$$\begin{aligned}
\hat{\eta}_{pr}^{qs} &= \hat{\eta}_p^q\hat{\eta}_r^s - \delta_{ps}\hat{\eta}_r^q \qquad (4.21)\\
&= (\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}} + \hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}})(\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}} + \hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}) - \delta_{ps}(\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{r}} + \hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{r}}) \qquad (4.22)\\
&= \hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}} + \hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}} + \hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}} + \hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}} - \delta_{\underline{ps}}\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{r}} - \delta_{\overline{ps}}\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{r}} \, . \qquad (4.23)
\end{aligned}$$

Using WICK's first theorem, eq. 4.23 can be recast in normal order as

$$\begin{aligned}
\hat{\eta}_{pr}^{qs} =&\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + \delta_{\underline{ps}\in\underline{\mathbb{V}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{r}}\} + \delta_{\underline{qr}\in\underline{\mathbb{O}}}\{\hat{a}_{\underline{p}}\hat{a}^\dagger_{\underline{s}}\} + \delta_{\underline{rs}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\} + \delta_{\underline{pq}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\}\\
&+ \delta_{\underline{pq}\in\underline{\mathbb{O}}}\delta_{\underline{rs}\in\underline{\mathbb{O}}} + \delta_{\underline{qr}\in\underline{\mathbb{O}}}\delta_{\underline{ps}\in\underline{\mathbb{V}}} + \{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + \delta_{\underline{p}\overline{s}\in\tilde{\mathbb{V}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\overline{r}}\} + \delta_{\underline{q}\overline{r}\in\tilde{\mathbb{O}}}\{\hat{a}_{\underline{p}}\hat{a}^\dagger_{\overline{s}}\}\\
&+ \delta_{\overline{rs}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\} + \delta_{\underline{pq}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + \delta_{\underline{pq}\in\underline{\mathbb{O}}}\delta_{\overline{rs}\in\overline{\mathbb{O}}} + \delta_{\underline{q}\overline{r}\in\tilde{\mathbb{O}}}\delta_{\underline{p}\overline{s}\in\tilde{\mathbb{V}}} + \{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\}\\
&+ \delta_{\overline{p}\underline{s}\in\tilde{\mathbb{V}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\underline{r}}\} + \delta_{\overline{q}\underline{r}\in\tilde{\mathbb{O}}}\{\hat{a}_{\overline{p}}\hat{a}^\dagger_{\underline{s}}\} + \delta_{\underline{rs}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\} + \delta_{\overline{pq}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + \delta_{\overline{pq}\in\overline{\mathbb{O}}}\delta_{\underline{rs}\in\underline{\mathbb{O}}}\\
&+ \delta_{\overline{q}\underline{r}\in\tilde{\mathbb{O}}}\delta_{\overline{p}\underline{s}\in\tilde{\mathbb{V}}} + \{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + \delta_{\overline{ps}\in\overline{\mathbb{V}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{r}}\} + \delta_{\overline{qr}\in\overline{\mathbb{O}}}\{\hat{a}_{\overline{p}}\hat{a}^\dagger_{\overline{s}}\} + \delta_{\overline{rs}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\}\\
&+ \delta_{\overline{pq}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + \delta_{\overline{pq}\in\overline{\mathbb{O}}}\delta_{\overline{rs}\in\overline{\mathbb{O}}} + \delta_{\overline{qr}\in\overline{\mathbb{O}}}\delta_{\overline{ps}\in\overline{\mathbb{V}}} - \delta_{\underline{ps}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{r}}\} - \delta_{\underline{ps}}\delta_{\underline{qr}\in\underline{\mathbb{O}}}\\
&- \delta_{\overline{ps}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{r}}\} - \delta_{\overline{ps}}\delta_{\overline{qr}\in\overline{\mathbb{O}}} \, . \qquad (4.24)
\end{aligned}$$

After eliminating the spin-opposite index combinations in the KRONECKER symbols, eq. 4.24 reads

$$\begin{aligned}
\hat{\eta}_{pr}^{qs} =&\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + {\color{red}\delta_{\underline{ps}\in\underline{\mathbb{V}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{r}}\}} + \delta_{\underline{qr}\in\underline{\mathbb{O}}}\{\hat{a}_{\underline{p}}\hat{a}^\dagger_{\underline{s}}\} + \delta_{\underline{rs}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\} + \delta_{\underline{pq}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\}\\
&+ \delta_{\underline{pq}\in\underline{\mathbb{O}}}\delta_{\underline{rs}\in\underline{\mathbb{O}}} + {\color{green}\delta_{\underline{qr}\in\underline{\mathbb{O}}}\delta_{\underline{ps}\in\underline{\mathbb{V}}}} + \{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + \delta_{\overline{rs}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\} + \delta_{\underline{pq}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\}\\
&+ \delta_{\underline{pq}\in\underline{\mathbb{O}}}\delta_{\overline{rs}\in\overline{\mathbb{O}}} + \{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + \delta_{\underline{rs}\in\underline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\} + \delta_{\overline{pq}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + \delta_{\overline{pq}\in\overline{\mathbb{O}}}\delta_{\underline{rs}\in\underline{\mathbb{O}}}\\
&+ \{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + {\color{blue}\delta_{\overline{ps}\in\overline{\mathbb{V}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{r}}\}} + \delta_{\overline{qr}\in\overline{\mathbb{O}}}\{\hat{a}_{\overline{p}}\hat{a}^\dagger_{\overline{s}}\} + \delta_{\overline{rs}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\} + \delta_{\overline{pq}\in\overline{\mathbb{O}}}\{\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\}\\
&+ \delta_{\overline{pq}\in\overline{\mathbb{O}}}\delta_{\overline{rs}\in\overline{\mathbb{O}}} + {\color{magenta}\delta_{\overline{qr}\in\overline{\mathbb{O}}}\delta_{\overline{ps}\in\overline{\mathbb{V}}}} - {\color{red}\delta_{\underline{ps}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{r}}\}} - {\color{green}\delta_{\underline{ps}}\delta_{\underline{qr}\in\underline{\mathbb{O}}}} - {\color{blue}\delta_{\overline{ps}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{r}}\}}\\
&- {\color{magenta}\delta_{\overline{ps}}\delta_{\overline{qr}\in\overline{\mathbb{O}}}} \, . \qquad (4.25)
\end{aligned}$$

Assuming $\tilde{\mathbb{o}} \cap \tilde{\mathbb{v}} = \emptyset$ allows for taking differences of the colored parts in eq. 4.25, as e.g. $\delta_{.\tilde{p}\tilde{q}\in\tilde{\mathbb{v}}} - \delta_{\tilde{p}\tilde{q}} = \delta_{\tilde{p}\tilde{q}\in\tilde{\mathbb{o}}}$ for non overlapping sets of occupied and virtual orbitals,

$$\begin{aligned}
\hat{\eta}^{qs}_{pr} =& \{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + \delta_{\underline{ps}\in\underline{\mathbb{o}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{r}}\} + \delta_{\underline{qr}\in\underline{\mathbb{o}}}\{\hat{a}_{\underline{p}}\hat{a}^\dagger_{\underline{s}}\} + \delta_{\underline{rs}\in\underline{\mathbb{o}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\} + \delta_{\underline{pq}\in\underline{\mathbb{o}}}\{\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} \\
&+ \delta_{\underline{pq}\in\underline{\mathbb{o}}}\delta_{\underline{rs}\in\underline{\mathbb{o}}} + \delta_{\underline{qr}\in\underline{\mathbb{o}}}\delta_{\underline{ps}\in\underline{\mathbb{o}}} + \{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + \delta_{\overline{rs}\in\overline{\mathbb{o}}}\{\hat{a}^\dagger_{\underline{q}}\hat{a}_{\underline{p}}\} + \delta_{\underline{pq}\in\underline{\mathbb{o}}}\{\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} \\
&+ \delta_{\underline{pq}\in\underline{\mathbb{o}}}\delta_{\overline{rs}\in\overline{\mathbb{o}}} + \{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + \delta_{\underline{rs}\in\underline{\mathbb{o}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\} + \delta_{\overline{pq}\in\overline{\mathbb{o}}}\{\hat{a}^\dagger_{\underline{s}}\hat{a}_{\underline{r}}\} + \delta_{\overline{pq}\in\overline{\mathbb{o}}}\delta_{\underline{rs}\in\underline{\mathbb{o}}} \\
&+ \{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} + \delta_{\overline{ps}\in\overline{\mathbb{o}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{r}}\} + \delta_{\overline{qr}\in\overline{\mathbb{o}}}\{\hat{a}_{\overline{p}}\hat{a}^\dagger_{\overline{s}}\} + \delta_{\overline{rs}\in\overline{\mathbb{o}}}\{\hat{a}^\dagger_{\overline{q}}\hat{a}_{\overline{p}}\} + \delta_{\overline{pq}\in\overline{\mathbb{o}}}\{\hat{a}^\dagger_{\overline{s}}\hat{a}_{\overline{r}}\} \\
&+ \delta_{\overline{pq}\in\overline{\mathbb{o}}}\delta_{\overline{rs}\in\overline{\mathbb{o}}} - \delta_{\overline{ps}\in\overline{\mathbb{o}}}\delta_{\overline{qr}\in\overline{\mathbb{o}}} \ . \qquad (4.26)
\end{aligned}$$

At first, the uncontracted terms of the last equation will be investigated. It turns out that they can be factorized into a product of substitutions. One obtains the normal ordered two particle part of the hamiltonian:

$$\hat{V}_N = \frac{1}{2}\sum_{pqrs} v^{qs}_{pr}\{\hat{\eta}^q_p\hat{\eta}^s_r\}, \qquad (4.27)$$

where the prefactor of one half stems from the particle symmetry.

Turning to the singly contracted terms one faces two contraction patterns: Contractions of p and q (or by interchanging dummy indices, r and s) and contractions of p and r (or again, q and s). Gathering these terms individually and using the antisymmetry of normal ordered operator strings, one obtains an effective one particle operator:

$$\begin{aligned}
2\hat{J} - \hat{K} &= \frac{1}{2}\sum_{ipq}(4v^{iq}_{ip} - 2v^{qi}_{ip})\{\hat{\eta}^q_p\} && (4.28) \\
&= \sum_{ipq}(2v^{iq}_{ip} - v^{qi}_{ip})\{\hat{\eta}^q_p\} \ . && (4.29)
\end{aligned}$$

This operator is combined with the non-scalar part of eq. 4.20 to yield the normal ordered Fock operator:

$$\hat{F}_N = \sum_{pg} \underbrace{\left(h^q_p + \sum_i 2v^{iq}_{ip} - v^{qi}_{ip}\right)}_{f^q_p}\{\hat{\eta}^q_p\} \ . \qquad (4.30)$$

It is remarkable that the integral part in eq. 4.30 exactly resembles the restricted HF integrals.

As a last step the scalar part of the normal ordered two particle operator will be investigated. Again two contraction patterns[1] are observed. Substituting spin orbital by spatial orbital indices and gathering terms yields

$$\begin{aligned}
2J - K &= \frac{1}{2}\sum_{ij}\left(4v^{ij}_{ij} - 2v^{ji}_{ij}\right) && (4.31) \\
&= \sum_{ij}\left(2v^{ij}_{ij} - v^{ji}_{ij}\right) \ . && (4.32)
\end{aligned}$$

[1] i.e. contractions with and without crossings.

This result will be combined with the scalar part of eq. 4.20. As a result one obtains the restricted HF energy expression

$$E_{\mathrm{RHF}} = 2\sum_i h_i^i + \sum_{ij} \left(2v_{ij}^{ij} - v_{ij}^{ji}\right) \ . \tag{4.33}$$

Following the investigation above the hamiltonian can be partitioned in the following way:

$$\hat{H} = \hat{F}_N + \hat{V}_N + E_{\mathrm{(R)HF}} \ . \tag{4.34}$$

It is now proven that the spin orbital and the spin independent hamiltonians show the same partitioning in normal ordered parts and scalar parts, where of course the integrals and energies have to be taken from the suited one particle method.

While this partition is known for the spin orbital case for a long time and can be found in several textbooks a similar derivation for the spin independent case is not known to the author[2].

4.3 Commutator Based Term Simplification Framework

In the last section the standard approach to the term simplification via Wick's theorems was focused. It is possible to formulate an alternative term simplification based on commutator relations for second quantized substitution operators. This concept will be the main topic of the following section. For convenience, a closed shell single reference wavefunction (e.g. a RHF ground state determinant) is assumed throughout the discussion in this section.

4.3.1 Spatial Orbital Substitution Operators in Wick's Theorem

To make use of the concept of second quantization, equation 4.7 can be employed to express the spatial orbital substitution operators in terms of annihilators and creators:

$$\hat{\eta}_p^q = \hat{a}_{\underline{q}}^\dagger \hat{a}_{\underline{p}} + \hat{a}_{\overline{q}}^\dagger \hat{a}_{\overline{p}} \ . \tag{4.35}$$

In principle it is now possible to apply the concept of normal order and subsequently Wick's theorems to simplify expressions involving spatial orbital substitution operators. However, inspection of the relation between the spatial orbital substitution operators and the second quantized creators and annihilators reveals that for every substitution the number of terms that have to be brought in normal order and then to be contracted increases by a factor of two[3].

[2] Despite the fact that it is very useful and probably also needed for the derivation of the coupled cluster working equations that are already implemented in common quantum chemistry software.

[3] Obviously this factor arises from the fact that $\hat{\eta}_p^q$ is the sum of two spin orbital substitution operators.

As a simple example a part of the CCSD doubles projections will be considered:

$$\langle \Phi_{IJ}^{AB} | e^{-\hat{E}_2} \hat{V}_N e^{\hat{E}_2} | \Phi_0 \rangle \quad \longleftarrow \quad \left\langle \Phi_0 \left| \hat{\eta}_A^I \hat{\eta}_B^J \hat{\eta}_p^q \hat{\eta}_r^s \hat{\eta}_i^a \hat{\eta}_j^b \;\; \Phi_0 \right\rangle \right. . \tag{4.36}$$

In the right hand side term six single orbital substitution operators arise (the fact that multiple orbital substitution operators can be decomposed will be discussed below) leading to $2^6 = 64$ products of annihilators and creators. An alternative to the standard approach of term simplification is needed to damp the effect of the splitting of the orbitals substitution operators into two addends.

4.3.2 Evaluation of Nested Commutator Expressions

In this section a few, for themselves rather simple, formulae will be investigated that together form the algebraic framework developed in this work.

First of all, as already pointed out, the space of single substitution operators is closed under the action of the commutator, i.e.

$$[\,,\,] : \{\sigma_p^q\} \times \{\sigma_p^q\} \longrightarrow \{\sigma_p^q\} \tag{4.37}$$

is a well defined, bilinear and antisymmetric map. Due to this the number of single substituters in a term decreases by one for each commutator expression involved according to

$$[\hat{\sigma}_p^q, \hat{\sigma}_r^s] = \delta_{ps} \hat{\sigma}_r^q - \delta_{rq} \hat{\sigma}_p^s \, . \tag{I}$$

This is, in fact, the commutator analogue to the contraction operation exploited in WICK's theorem.

In order to apply the reduction of the number of operators, the commutators have to be brought in a special form. Since only a formula for commutators containing two single substituters is available, an expansion of commutators of products is needed. This expansion formula can easily be derived and proven by induction:

$$[\hat{A}, \hat{B}_1 \ldots \hat{B}_n] = \sum_{k=1}^{n} \hat{B}_1 \ldots \hat{B}_{k-1} [\hat{A}, \hat{B}_k] \hat{B}_{k+1} \ldots \hat{B}_n \, . \tag{II}$$

A combination of eqs. 4.37 and II to an example term yields:

$$[\hat{\sigma}_p^q, \hat{\sigma}_{i_1}^{a_1} \hat{\sigma}_{i_2}^{a_2} \ldots \hat{\sigma}_{i_n}^{a_n}] = \sum_{k=1}^{n} \hat{\sigma}_{i_1}^{a_1} \ldots \hat{\sigma}_{i_{k-1}}^{a_{k-1}} [\hat{\sigma}_p^q, \sigma_{i_k}^{a_k}] \hat{\sigma}_{i_{k+1}}^{a_{k+1}} \ldots \hat{\sigma}_{i_n}^{a_n} \tag{4.38}$$

$$= \sum_{k=1}^{n} \delta_{pa_k} \hat{\sigma}_{i_1}^{a_1} \ldots \hat{\sigma}_{i_{k-1}}^{a_{k-1}} \hat{\sigma}_{i_k}^{q} \hat{\sigma}_{i_{k+1}}^{a_{k+1}} \ldots \hat{\sigma}_{i_n}^{a_n}$$

$$- \sum_{k=1}^{n} \delta_{i_k q} \hat{\sigma}_{i_1}^{a_1} \ldots \hat{\sigma}_{i_{k-1}}^{a_{k-1}} \hat{\sigma}_{p}^{a_k} \hat{\sigma}_{i_{k+1}}^{a_{k+1}} \ldots \hat{\sigma}_{i_n}^{a_n} \, . \tag{4.39}$$

It turns out that a straightforward application of these two rules is not sufficient for a full simplification of the operator strings as can be seen from the previous equation. Additional rules for the generation of new commutator expressions are needed.

Since in the linked form of coupled cluster, all expressions are evaluated as Fermi vacuum expectation values, the following two equations hold:

$$\langle\Phi_0|\hat{\sigma}_p^a\hat{\sigma}_q^s\ldots\;\Phi_0\rangle = 0 \tag{4.40}$$

and

$$\langle\Phi_0|\ldots\hat{\sigma}_p^q\hat{\sigma}_a^s\;\Phi_0\rangle = 0\;. \tag{4.41}$$

This is due to the fact that in the upper equation a particle creator acts on the bra state while in the lower equation a particle annihilator acts on the ket state. When the permuted products of the above expressions is subtracted (and the sign is inverted) one obtains:

$$-\langle\Phi_0|\hat{\sigma}_p^a\hat{\sigma}_q^s\ldots\;\Phi_0\rangle + \langle\Phi_0|\hat{\sigma}_q^s\hat{\sigma}_p^a\ldots\;\Phi_0\rangle = \langle|\hat{\sigma}_q^s\hat{\sigma}_p^a\ldots\;\Phi_0\rangle \tag{4.42}$$

and

$$-\langle\Phi_0|\Phi_0\ldots\hat{\sigma}_p^q\hat{\sigma}_a^s\;\Phi_0\rangle + \langle\Phi_0|\ldots\hat{\sigma}_a^s\hat{\sigma}_p^q\;\Phi_0\rangle = \langle\Phi_0|\ldots\hat{\sigma}_a^s\hat{\sigma}_p^q\;\Phi_0\rangle\,, \tag{4.43}$$

or equivalently written as commutator expressions:

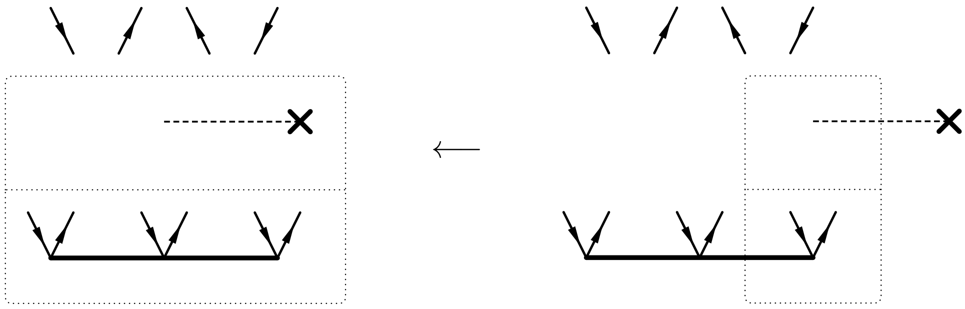
$$\langle\Phi_0|[\hat{\sigma}_q^s,\hat{\sigma}_p^a]\ldots\;\Phi_0\rangle = \langle\Phi_0|\hat{\sigma}_q^s\hat{\sigma}_p^a\ldots\;\Phi_0\rangle \tag{IIIa}$$

and

$$\langle\Phi_0|\ldots[\hat{\sigma}_a^s,\sigma_p^q]\;\Phi_0\rangle = \langle\Phi_0|\ldots\hat{\sigma}_a^s\hat{\sigma}_p^q\;\Phi_0\rangle\;. \tag{IIIb}$$

The last two equations now represent a rule to substitute suited operator products by commutator expressions.

By means of the eqs. I, II, IIa and IIb an algorithm for the term simplification can be derived. Since the algorithm will be discussed in detail in the following chapter, only a short note on its workflow will be given here. Starting from a nested commutator expression (as e.g. the BCH formula) an expansion emloying eq. II is applied. The iterative application of eq. I on the resulting expression itself generates equations whithout any commutators, but involving shorter operator strings. After this step new commutators are generated by means of eqs. IIIa or IIIb. The overal procedure is repeated until there is no change in the expression anymore. Examples for the application of this algorithm are given in the next section alongside diagrammatic representations.



$$\tfrac{1}{6}\left\langle \Phi_0 \left| \hat{\sigma}^I_A \hat{\sigma}^J_B \left[\hat{\sigma}^q_p, \hat{\sigma}^{abc}_{ijk}\right] \right. \Phi_0 \right\rangle \quad \longleftarrow \quad \tfrac{1}{6}\left\langle \Phi_0 \left| \hat{\sigma}^I_A \hat{\sigma}^J_B \hat{\sigma}^a_i \hat{\sigma}^b_j \left[\hat{\sigma}^q_p, \hat{\sigma}^c_k\right] \right. \Phi_0 \right\rangle$$

Figure 4.1: Diagrammatic representation of the initial expansion step of the algebraic term simplification.

4.3.3 Diagrammatic Representation

The algebraic term simplification presented can also be reformulated employing coupled cluster diagrams. A striking feature of the approach is that one can start from diagram fragments depicting the operators to be contracted. A commutator of operators will be depicted by a dotted polygonal line surrounding the operators, which is divided into two regions representing the left and right hand side entries of the commutator, respectively. From this starting point the diagram connections are built up step by step.

4.3.3.1 Example Involving Triple Excitations

In the diagrammatic version the commutators connecting certain operator strings are depicted by dotted polygons surrounding these. The polygons are subdivided by a dotted line that separates the two positions in the commutator (cf. fig. 4.1, left hand side).

The example depicted here has the algebraic form of a double projection of a commutator of the Fock operator and a triple excitation (the tensor quantities associated to the operators have been omittet, please note that lower case indices are to be summed over):

$$\left\langle \Phi_0 \left| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3\right] \right. \Phi_0 \right\rangle = \frac{1}{6} \left\langle \Phi_0 \left| \hat{\sigma}^I_A \hat{\sigma}^J_B \left[\hat{\sigma}^q_p, \hat{\sigma}^a_i \hat{\sigma}^b_j \hat{\sigma}^c_k\right] \right. \Phi_0 \right\rangle \ . \tag{4.44}$$

The expansion of the commutator presented in eq. 4.44 according to eq. II in principle yields three terms. The focus in this discussion will be laid upon the following term:

$$\left\langle \Phi_0 \left| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3\right] \right. \Phi_0 \right\rangle \longleftarrow \frac{1}{6} \left\langle \Phi_0 \left| \hat{\sigma}^I_A \hat{\sigma}^J_B \hat{\sigma}^a_i \hat{\sigma}^b_j \left[\hat{\sigma}^q_p, \hat{\sigma}^c_k\right] \right. \Phi_0 \right\rangle \ , \tag{4.45}$$

as depicted on the right hand side of fig. 4.1. The commutator polygon in this figure now only includes the right hand side part of the $\hat{T}_3$ operator fragment. Of course, the remaining two terms are to be depicted with the innermost polygon including the middle and the left parts only, respectively. The evaluation of the commutator expression yields two possible contraction patterns:

$$\left\langle \Phi_0 \middle| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3 \right] \ \Phi_0 \right\rangle \longleftarrow \frac{1}{6} \left\langle \Phi_0 \left| \hat{\sigma}^I_A \hat{\sigma}^J_B \hat{\sigma}^a_i \hat{\sigma}^b_j \big(\delta_{pc} \hat{\sigma}^q_k - \delta_{kq} \hat{\sigma}^c_p \big) \ \Phi_0 \right. \right\rangle \ . \tag{4.46}$$

The following discussion will concentrate on the further evaluation of the particle contraction:

$$\left\langle \Phi_0 \middle| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3 \right] \ \Phi_0 \right\rangle \longleftarrow \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| \hat{\sigma}^I_A \hat{\sigma}^J_B \hat{\sigma}^a_i \hat{\sigma}^b_j \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle \ . \tag{4.47}$$

In eq. 4.47 a new nested commutator expression can be generated according to eq. IIIa, yielding (cf. also fig. 4.2):

$$\left\langle \Phi_0 \middle| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3 \right] \ \Phi_0 \right\rangle \longleftarrow \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| [[\hat{\sigma}^I_A \hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle \ . \tag{4.48}$$

Eq. IIIa was chosen for the commutator generation only as a matter of taste. Alternatively one could also generate new commutators employing the projections, leaving the final result unaltered.

The next step is again a simple expansion by means of eq. II resulting in four terms including only single substitution operator commutators:

$$\begin{aligned} \left\langle \Phi_0 \middle| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3 \right] \ \Phi_0 \right\rangle \longleftarrow & \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| \hat{\sigma}^I_A [[\hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle \\ & + \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| [\hat{\sigma}^I_A, \hat{\sigma}^b_j][\hat{\sigma}^J_B, \hat{\sigma}^a_i] \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle \\ & + \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| [\hat{\sigma}^I_A, \hat{\sigma}^a_i][\hat{\sigma}^J_B, \hat{\sigma}^b_j] \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle \\ & + \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| [[\hat{\sigma}^I_A, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \hat{\sigma}^J_B \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle \ . \end{aligned} \tag{4.49}$$

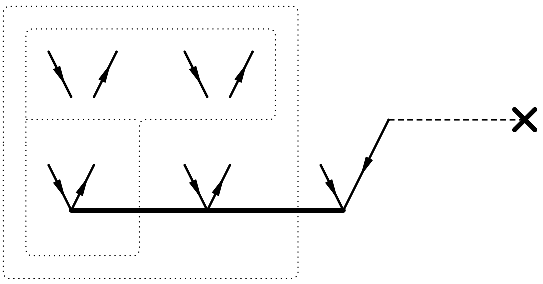
The second term of this expansion is depicted in fig. 4.3 in a diagrammatic way.[4]

Upon closer inspection of fig. 4.3 one can see that the polygons depicting the commutators now include only single pairs of particle and hole lines, which is the graphical analogue to the fact that the innermost commutators contain single substitution operators only. It is now possible to employ eq. 4.37 to reduce the number of substituters and simultaneously contract two vertices in every polygon. The result of this action is given by:

$$\left\langle \Phi_0 \middle| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3 \right] \ \Phi_0 \right\rangle \leftarrow \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| [\hat{\sigma}^I_A, \hat{\sigma}^b_j][\hat{\sigma}^J_B, \hat{\sigma}^a_i] \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle \tag{4.50}$$

$$\leftarrow \frac{1}{6} \delta_{pc} \left\langle \Phi_0 \left| (\delta_{Ab} \hat{\sigma}^I_j - \delta_{jI} \hat{\sigma}^b_A)(\delta_{Ba} \hat{\sigma}^J_i - \delta_{iJ} \hat{\sigma}^a_B) \hat{\sigma}^q_k \ \Phi_0 \right. \right\rangle . \tag{4.51}$$

[4] For reasons of tensor symmetry the third term shares the depicted diagram. The algebraic coincidence of the two terms becomes clear upon a $i \rightarrow j, a \rightarrow b$ exchange.



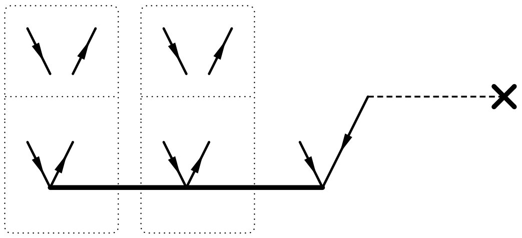
$$\tfrac{1}{6}\delta_{pc}\left\langle\Phi_0\left|[[\hat{\sigma}^I_A\hat{\sigma}^J_B,\hat{\sigma}^a_i],\hat{\sigma}^b_j]\hat{\sigma}^k_q\ \ \Phi_0\right.\right\rangle$$

Figure 4.2: Diagrammatic representation of an already singly contracted term turning up as an intermediate.

The second term in the first factor of the previous equation vanishes due to an upper left particle creator. The remaining two terms read:

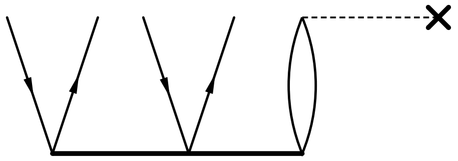
$$\begin{aligned}\left\langle\Phi_0\left|\hat{D}_2\left[\hat{F}_N,\hat{T}_3\right]\ \ \Phi_0\right.\right\rangle \longleftarrow\ & \frac{1}{6}\delta_{pc}\delta_{Ab}\delta_{Ba}\left\langle\Phi_0\left|\hat{\sigma}^I_j\hat{\sigma}^J_i\hat{\sigma}^q_k\ \ \Phi_0\right.\right\rangle\\ & -\frac{1}{6}\delta_{pc}\delta_{Ab}\delta_{iJ}\left\langle\Phi_0\left|\hat{\sigma}^I_j\hat{\sigma}^a_B\hat{\sigma}^q_k\ \ \Phi_0\right.\right\rangle\ . \qquad (4.52)\end{aligned}$$

The second term of eq. 4.52 can again be transformed into a commutator expression, but, involving the due to mismatching indices uncontractable commutator $[\hat{\sigma}^I_j,\hat{\sigma}^a_B]$, it clearly vanishes.



$$\tfrac{1}{6}\delta_{pc}\left\langle\Phi_0\left|[\hat{\sigma}^I_A,\hat{\sigma}^b_j][\hat{\sigma}^J_B,\hat{\sigma}^a_i]\hat{\sigma}^q_k\ \ \Phi_0\right.\right\rangle$$

Figure 4.3: Diagrammatic representation of an intermediate term containing two non-nested commutators.



$$\frac{a_s^3}{6}\sum_{ia} f_i^a t_{iIJ}^{aAB}$$

Figure 4.4: Diagrammatic representation of a fully contracted term.

The final step in term simplification is the evaluation of the remaining uncontracted substitution operators. A special attention has to be paid to the occurring spin integration factors arising.

For every single substitution operator upon contraction, a prefactor of a_s has to be inserted, which is one in the spin orbital picture and two for the spatial orbital picture due to the two possible matching spin combinations, namely $\alpha-\alpha$ and $\beta-\beta$. This results in the final fully contracted term

$$\left\langle \Phi_0 \middle| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3\right] \ \Phi_0 \right\rangle \longleftarrow \frac{a_s^3}{6}\delta_{pc}\delta_{Ab}\delta_{Ba}\delta_{jI}\delta_{iJ}\delta_{kq}\,, \tag{4.53}$$

or in a tensor sum of product manner:

$$\left\langle \Phi_0 \middle| \hat{D}_2 \left[\hat{F}_N, \hat{T}_3\right] \ \Phi_0 \right\rangle \longleftarrow \frac{a_s^3}{6}\sum_{ia} f_i^a t_{iIJ}^{aAB}\ . \tag{4.54}$$

The diagrammatic representation of this term can be seen in fig. 4.4.

4.3.3.2 A Note on Tensor Symmetries

A fact that could already be seen in the derivation of the normal ordered hamiltonian in the spatial orbital picture is the special symmetry of the tensor quantities in this framework. It is, however, easier to discuss this feature in a diagrammatic context. As an example for the different symmetry properties of spin and spatial orbital picture tensor quantities the term

$$\begin{aligned}
\left\langle \Phi_0 \middle| \hat{D}_1^\dagger [\hat{F}_N, \hat{T}_2] \ \Phi_0 \right\rangle &= \frac{1}{2}\left\langle \Phi_0 \middle| \hat{\sigma}_A^I [\hat{\sigma}_p^q, \hat{\sigma}_i^a \hat{\sigma}_j^b] \ \Phi_0 \right\rangle && (4.55)\\
&= \frac{1}{2}\left\langle \Phi_0 \middle| \left[\hat{\sigma}_A^I, [\hat{\sigma}_p^q, \hat{\sigma}_i^a \hat{\sigma}_j^b]\right] \ \Phi_0 \right\rangle && (4.56)
\end{aligned}$$

will be investigated. Its expansion into commutators involving only single substituters yields four terms, namely:

$$\begin{aligned}
\left\langle \Phi_0 \middle| \hat{D}_1^\dagger [\hat{F}_N, \hat{T}_2] \;\; \Phi_0 \right\rangle = \; & \frac{1}{2} \left\langle \Phi_0 \middle| \hat{\sigma}_i^a \left[\hat{\sigma}_A^I, [\hat{\sigma}_p^q, \hat{\sigma}_j^b] \right] \;\; \Phi_0 \right\rangle \\
& + \frac{1}{2} \left\langle \Phi_0 \middle| \left[\hat{\sigma}_A^I, [\hat{\sigma}_p^q, \hat{\sigma}_i^a] \right] \hat{\sigma}_j^b \;\; \Phi_0 \right\rangle \\
& + \frac{1}{2} \left\langle \Phi_0 \middle| [\hat{\sigma}_A^I, \hat{\sigma}_i^a][\hat{\sigma}_p^q, \hat{\sigma}_j^b] \;\; \Phi_0 \right\rangle \\
& + \frac{1}{2} \left\langle \Phi_0 \middle| [\hat{\sigma}_p^q, \hat{\sigma}_i^a][\hat{\sigma}_A^I, \hat{\sigma}_j^b] \;\; \Phi_0 \right\rangle \; .
\end{aligned} \tag{4.57}$$

The first of these terms obviously vanishes in the FERMI vacuum expectation value, while the last term can be written as a triply nested commutator via eq. IIIb:

$$\begin{aligned}
\left\langle \Phi_0 \middle| \hat{D}_1^\dagger [\hat{F}_N, \hat{T}_2] \;\; \Phi_0 \right\rangle = \; & \frac{1}{2} \left\langle \Phi_0 \middle| \left[\left[\hat{\sigma}_A^I, [\hat{\sigma}_p^q, \hat{\sigma}_i^a] \right], \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle \\
& + \frac{1}{2} \left\langle \Phi_0 \middle| [\hat{\sigma}_A^I, \hat{\sigma}_i^a][\hat{\sigma}_p^q, \hat{\sigma}_j^b] \;\; \Phi_0 \right\rangle \\
& + \frac{1}{2} \left\langle \Phi_0 \middle| [\hat{\sigma}_p^q, \hat{\sigma}_i^a][\hat{\sigma}_A^I, \hat{\sigma}_j^b] \;\; \Phi_0 \right\rangle \; .
\end{aligned} \tag{4.58}$$

The first of the three remaining terms can be expanded as follows:

$$\begin{aligned}
\frac{1}{2} \left\langle \Phi_0 \middle| \left[\left[\hat{\sigma}_A^I, [\hat{\sigma}_p^q, \hat{\sigma}_i^a] \right], \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle = \; & \frac{1}{2} \delta_{pa} \left\langle \Phi_0 \middle| \left[\left[\hat{\sigma}_A^I, \hat{\sigma}_i^q \right], \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle \\
& - \frac{1}{2} \left\langle \Phi_0 \middle| \delta_{iq} \left[\left[\hat{\sigma}_A^I, \hat{\sigma}_p^a \right], \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle
\end{aligned} \tag{4.59}$$

$$\begin{aligned}
= \; & \frac{1}{2} \delta_{pa} \delta_{Aq} \left\langle \Phi_0 \middle| \left[\hat{\sigma}_i^I, \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle \\
& - \frac{1}{2} \delta_{pa} \delta_{iI} \left\langle \Phi_0 \middle| \left[\hat{\sigma}_A^q, \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle \\
& - \frac{1}{2} \delta_{iq} \delta_{Aa} \left\langle \Phi_0 \middle| \left[\hat{\sigma}_p^I, \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle \\
& + \frac{1}{2} \delta_{iq} \delta_{pI} \left\langle \Phi_0 \middle| \left[\hat{\sigma}_A^a, \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle \; .
\end{aligned} \tag{4.60}$$

The first and last term of this equation vanish upon expansion because of contractions between particles and holes or generation of a particle creator as upper left index. The further evaluation thus simplifies to:

$$\begin{aligned}
\frac{1}{2} \left\langle \Phi_0 \middle| \left[\left[\hat{\sigma}_A^I, [\hat{\sigma}_p^q, \hat{\sigma}_i^a] \right], \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle = \; & -\frac{1}{2} \delta_{pa} \delta_{iI} \left\langle \Phi_0 \middle| \left[\hat{\sigma}_A^q, \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle \\
& - \frac{1}{2} \delta_{iq} \delta_{Aa} \left\langle \Phi_0 \middle| \left[\hat{\sigma}_p^I, \hat{\sigma}_j^b \right] \;\; \Phi_0 \right\rangle
\end{aligned} \tag{4.61}$$

$$\begin{aligned}
= \; & -\frac{1}{2} \delta_{pa} \delta_{iI} \delta_{Ab} \left\langle \Phi_0 \middle| \hat{\sigma}_j^q \;\; \Phi_0 \right\rangle \\
& - \frac{1}{2} \delta_{iq} \delta_{Aa} \delta_{pb} \left\langle \Phi_0 \middle| \hat{\sigma}_j^I \;\; \Phi_0 \right\rangle \; .
\end{aligned} \tag{4.62}$$

The second term of 4.58 can be written as:

$$\begin{aligned}\frac{1}{2}\left\langle\Phi_0\left|[\hat{\sigma}^I_A,\hat{\sigma}^a_i][\hat{\sigma}^q_p,\hat{\sigma}^b_j]\ \ \Phi_0\right.\right\rangle &= \frac{1}{2}\left\langle\Phi_0\left|(\delta_{Aa}\hat{\sigma}^I_i-\delta_{iI}\hat{\sigma}^a_A)(\delta_{pb}\hat{\sigma}^q_j-\delta_{jq}\hat{\sigma}^b_p)\ \ \Phi_0\right.\right\rangle && (4.63)\\ &= \frac{1}{2}\delta_{Aa}\delta_{pb}\left\langle\Phi_0\left|\hat{\sigma}^I_i\hat{\sigma}^q_j\ \ \Phi_0\right.\right\rangle \\ &\quad -\frac{1}{2}\delta_{Aa}\delta_{jq}\left\langle\Phi_0\left|\hat{\sigma}^I_i\hat{\sigma}^b_p\ \ \Phi_0\right.\right\rangle\ , && (4.64)\end{aligned}$$

where the last term can be written as its commutator analogue:

$$\begin{aligned}\frac{1}{2}\left\langle\Phi_0\left|[\hat{\sigma}^I_A,\hat{\sigma}^a_i][\hat{\sigma}^q_p,\hat{\sigma}^b_j]\ \ \Phi_0\right.\right\rangle &= \frac{1}{2}\delta_{Aa}\delta_{pb}\left\langle\Phi_0\left|\hat{\sigma}^I_i\hat{\sigma}^q_j\ \ \Phi_0\right.\right\rangle \\ &\quad -\frac{1}{2}\delta_{Aa}\delta_{jq}\left\langle\Phi_0\left|[\hat{\sigma}^I_i,\hat{\sigma}^b_p]\ \ \Phi_0\right.\right\rangle && (4.65)\\ &= \frac{1}{2}\delta_{Aa}\delta_{pb}\left\langle\Phi_0\left|\hat{\sigma}^I_i\hat{\sigma}^q_j\ \ \Phi_0\right.\right\rangle \\ &\quad +\frac{1}{2}\delta_{Aa}\delta_{jq}\left\langle\Phi_0\left|\hat{\sigma}^b_i\ \ \Phi_0\right.\right\rangle && (4.66)\\ &= \frac{1}{2}\delta_{Aa}\delta_{pb}\left\langle\Phi_0\left|\hat{\sigma}^I_i\hat{\sigma}^q_j\ \ \Phi_0\right.\right\rangle\ . && (4.67)\end{aligned}$$

In a similar fashion the third term yields:

$$\frac{1}{2}\left\langle\Phi_0\left|[\hat{\sigma}^q_p,\hat{\sigma}^a_i][\hat{\sigma}^I_A,\hat{\sigma}^b_j]\ \ \Phi_0\right.\right\rangle = \frac{1}{2}\delta_{pa}\delta_{Ab}\left\langle\Phi_0\left|\hat{\sigma}^q_i\hat{\sigma}^I_j\ \ \Phi_0\right.\right\rangle\ . \qquad (4.68)$$

After a final WICK contraction of the remaining operators one obtains:

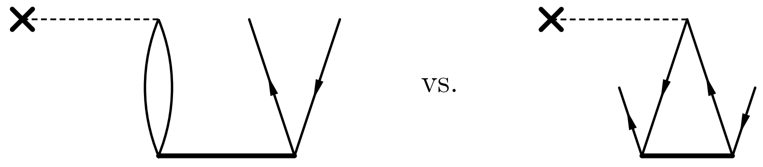
$$\begin{aligned}\left\langle\Phi_0\left|\hat{D}^\dagger_1[\hat{F}_N,\hat{T}_2]\ \ \Phi_0\right.\right\rangle &= \frac{1}{2}a_s^2\delta_{Aa}\delta_{pb}\delta_{i^I}\delta_{jq}+\frac{1}{2}a_s^2\delta_{pa}\delta_{Ab}\delta_{iq}\delta_{jI} \\ &\quad -\frac{1}{2}a_s\delta_{pa}\delta_{iI}\delta_{Ab}\delta_{jq}-\frac{1}{2}a_s\delta_{iq}\delta_{Aa}\delta_{pb}\delta_{jI}\ , && (4.69)\end{aligned}$$

where $a_s \in \{1,2\}$ is a spin integration factor for the spin orbital and the spin free picture, respectively.

The last step is to translate the contractions, now in form of KRONECKER symbol products, into the corresponding tensor equation (with canonical dummy indices):

$$\left\langle\Phi_0\left|\hat{D}^\dagger_1[\hat{F}_N,\hat{T}_2]\ \ \Phi_0\right.\right\rangle = \frac{1}{2}\sum_{ia} a_s^2 f^i_a t^{Aa}_{Ii} - a_s f^i_a t^{aA}_{Ii}\ . \qquad (4.70)$$

For the spin orbital picture the two terms coincide due to tensor antisymmetry, whereas for the spin free picture antisymmetry does not hold. One obtains two distinct terms, the first one weighted by a factor of two and the second one represented by a maximum loop rule violating diagram (cf. fig 4.5).



$\frac{1}{2}a_s^2\sum_{ia} f^i_a t^{Aa}_{Ii}$ vs. $-\frac{1}{2}a_s\sum_{ia} f^i_a t^{aA}_{Ii}$

Figure 4.5: Weighted and maximum loop rule violating diagrams for the singles projection of $[\hat{F}_N, \hat{T}_2]$.

4.3.3.3 Note on the Applicability to the CI Problem

The (truncated) configuration interaction problem is normally dealt with in a matrix algebra representation. However, it is also possible to represent the substitutions in their second quantized form to yield an equation system, which does not contain the commutator structure present in the Baker-Campbell-Hausdorff expansion occuring in the coupled cluster framework. The equation system reads:

$$\langle\Phi_0|\hat{D}_n^\dagger(\hat{H}_N - E)(1+\hat{C}_k)\ \Phi_0\rangle = 0, \qquad \forall_{k,n\in\{0,1,\ldots,n_\text{trunc}\}}\,, \tag{4.71}$$

where n_trunc is the truncation order and $\hat{D}_0^\dagger = \hat{C}_0 = \hat{I}$ are the identity operators.

In the second quantized representation the energy is dealt with as a simple rank zero tensor in the working equations. The algebraic term simplification via Wick's theorem, as well as the presented approach, can still be applied to the formal CI equations due to their similarity to the coupled cluster equations. Formally, the difference is only in the missing neccessity to apply the BCH expansion to the similarity transformed hamiltonian. This fact causes absolutely no difference in the application of Wick's theorem.

In the commutator evaluation approach presented in this work, it is convenient not to start with a commutator expansion step, but rather, at first generate suitable commutator expressions. In the following discussion, the right hand side of

$$\langle\Phi_0|\hat{D}_n^\dagger\hat{H}_N\hat{C}_n\ \Phi_0\rangle = \langle\Phi_0|\hat{D}_n^\dagger E\hat{C}_n\ \Phi_0\rangle, \qquad \forall_{n\in\{0,1,\ldots,n_\text{trunc}\}} \tag{4.72}$$

$$= E\langle\Phi_0|\hat{D}_2^\dagger\hat{C}_2\ \Phi_0\rangle \tag{4.73}$$

will be dealt with in the CID approximation. Explicitly written in terms of second quantized substituters, it reads:

$$E\langle\Phi_0|\hat{D}_2^\dagger\hat{C}_2\ \Phi_0\rangle = \frac{1}{2}E\langle\Phi_0|\hat{\sigma}_A^I\hat{\sigma}_B^J\hat{\sigma}_i^a\hat{\sigma}_j^b\ \Phi_0\rangle \tag{4.74}$$

$$= \frac{1}{2}E\langle\Phi_0|[[\hat{\sigma}_A^I\hat{\sigma}_B^J,\hat{\sigma}_i^a],\hat{\sigma}_j^b]\ \Phi_0\rangle\ . \tag{4.75}$$

The tensor quantities will be omitted in the following discussion as usual. One arrives at the following term to be simplified:

$$\begin{aligned}\left\langle \Phi_0 \middle| [[\hat{\sigma}^I_A \hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle &= \left\langle \Phi_0 \middle| [\hat{\sigma}^I_A [\hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| [[\hat{\sigma}^I_A, \hat{\sigma}^a_i] \hat{\sigma}^J_B, \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle \end{aligned} \tag{4.76}$$

$$\begin{aligned} &= \left\langle \Phi_0 \middle| \hat{\sigma}^I_A [[\hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| [\hat{\sigma}^I_A, \hat{\sigma}^b_j][\hat{\sigma}^J_B, \hat{\sigma}^a_i] \;\; \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| [\hat{\sigma}^I_A, \hat{\sigma}^a_i][\hat{\sigma}^J_B, \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| [[\hat{\sigma}^I_A, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \hat{\sigma}^J_B \;\; \Phi_0 \right\rangle \; . \end{aligned} \tag{4.77}$$

The last term obviously vanishes as well as the hole-hole contractions in the first factors of the second and third terms. This leads to the expression:

$$\begin{aligned}\left\langle \Phi_0 \middle| [[\hat{\sigma}^I_A \hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle &= \left\langle \Phi_0 \middle| \hat{\sigma}^I_A [(\delta_{Ba} \hat{\sigma}^J_i - \delta_{iJ} \hat{\sigma}^a_B), \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle \\ &\quad + \delta_{Ab} \left\langle \Phi_0 \middle| \hat{\sigma}^I_j [\hat{\sigma}^J_B, \hat{\sigma}^a_i] \;\; \Phi_0 \right\rangle \\ &\quad + \delta_{Aa} \left\langle \Phi_0 \middle| \hat{\sigma}^I_i [\hat{\sigma}^J_B, \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle \; . \end{aligned} \tag{4.78}$$

In the fist term of this equation only one contraction remains for each operator due to the non-overlapping particle and hole spaces. Expansion of all commutators leads to:

$$\begin{aligned}\left\langle \Phi_0 \middle| [[\hat{\sigma}^I_A \hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \;\; \Phi_0 \right\rangle &= \left\langle \Phi_0 \middle| \hat{\sigma}^I_A (-\delta_{Ba} \delta_{jJ} \hat{\sigma}^b_i - \delta_{iJ} \delta_{bB} \hat{\sigma}^a_j) \;\; \Phi_0 \right\rangle \\ &\quad + \delta_{Ab} \left\langle \Phi_0 \middle| \hat{\sigma}^I_j (\delta_{aB} \hat{\sigma}^J_i - \delta_{iJ} \hat{\sigma}^a_B) \;\; \Phi_0 \right\rangle \\ &\quad + \delta_{Aa} \left\langle \Phi_0 \middle| \hat{\sigma}^I_i (\delta_{bB} \hat{\sigma}^J_j - \delta_{jJ} \hat{\sigma}^b_B) \;\; \Phi_0 \right\rangle \end{aligned} \tag{4.79}$$

$$\begin{aligned} &= -\delta_{Ba} \delta_{jJ} \left\langle \Phi_0 \middle| \hat{\sigma}^I_A \hat{\sigma}^b_i \;\; \Phi_0 \right\rangle \\ &\quad - \delta_{iJ} \delta_{bB} \left\langle \Phi_0 \middle| \hat{\sigma}^I_A \hat{\sigma}^a_j \;\; \Phi_0 \right\rangle \\ &\quad + \delta_{Ab} \delta_{aB} \left\langle \Phi_0 \middle| \hat{\sigma}^I_j \hat{\sigma}^J_i \;\; \Phi_0 \right\rangle \\ &\quad - \delta_{Ab} \delta_{iJ} \left\langle \Phi_0 \middle| \hat{\sigma}^I_j \hat{\sigma}^a_B \;\; \Phi_0 \right\rangle \\ &\quad + \delta_{Aa} \delta_{bB} \left\langle \Phi_0 \middle| \hat{\sigma}^I_i \hat{\sigma}^J_j \;\; \Phi_0 \right\rangle \\ &\quad - \delta_{Aa} \delta_{jJ} \left\langle \Phi_0 \middle| \hat{\sigma}^I_i \hat{\sigma}^b_B \;\; \Phi_0 \right\rangle . \end{aligned} \tag{4.80}$$

After the expansion, new commutator expressions in the resulting terms can be sought. The third and fifth terms are not further contractable, while the fourth and sixth terms generate commutators with mismatching indices for contraction (and thus vanish). The new expression containing commutators can be written as:

$$\begin{aligned}
\left\langle \Phi_0 \left| [[\hat{\sigma}^I_A \hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \;\; \Phi_0 \right.\right\rangle &= -\delta_{Ba}\delta_{jJ} \left\langle \Phi_0 \left| [\hat{\sigma}^I_A, \hat{\sigma}^b_i] \;\; \Phi_0 \right.\right\rangle \\
&\quad - \delta_{iJ}\delta_{bB} \left\langle \Phi_0 \left| [\hat{\sigma}^I_A, \hat{\sigma}^a_j] \;\; \Phi_0 \right.\right\rangle \\
&\quad + \delta_{Ab}\delta_{aB} \left\langle \Phi_0 \left| \hat{\sigma}^I_j \hat{\sigma}^J_i \;\; \Phi_0 \right.\right\rangle \\
&\quad + \delta_{Aa}\delta_{bB} \left\langle \Phi_0 \left| \hat{\sigma}^I_i \hat{\sigma}^J_j \;\; \Phi_0 \right.\right\rangle \qquad (4.81) \\
&= -\delta_{Ba}\delta_{jJ}\delta_{Ab} \left\langle \Phi_0 \left| \hat{\sigma}^I_i \;\; \Phi_0 \right.\right\rangle \\
&\quad - \delta_{iJ}\delta_{bB}\delta_{Aa} \left\langle \Phi_0 \left| \hat{\sigma}^I_j \;\; \Phi_0 \right.\right\rangle \\
&\quad + \delta_{Ab}\delta_{aB} \left\langle \Phi_0 \left| \hat{\sigma}^I_j \hat{\sigma}^J_i \;\; \Phi_0 \right.\right\rangle \\
&\quad + \delta_{Aa}\delta_{bB} \left\langle \Phi_0 \left| \hat{\sigma}^I_i \hat{\sigma}^J_j \;\; \Phi_0 \right.\right\rangle \; . \qquad (4.82)
\end{aligned}$$

The final Wɪᴄᴋ contraction yields

$$\begin{aligned}
\left\langle \Phi_0 \left| [[\hat{\sigma}^I_A \hat{\sigma}^J_B, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \;\; \Phi_0 \right.\right\rangle &= -a_s\delta_{Ba}\delta_{jJ}\delta_{Ab}\delta_{iI} - a_s\delta_{iJ}\delta_{bB}\delta_{Aa}\delta_{jI} \\
&\quad + a_s^2\delta_{Ab}\delta_{aB}\delta_{jI}\delta_{iJ} + a_s^2\delta_{Aa}\delta_{bB}\delta_{iI}\delta_{jJ} \, , \qquad (4.83)
\end{aligned}$$

with the spin integration factor a_s, which results in the following tensor equation:

$$\begin{aligned}
E\langle\Phi_0|\hat{D}_2^\dagger \hat{C}_2 \;\Phi_0\rangle &= \frac{1}{2}E\left(-a_s c^{BA}_{IJ} - a_s c^{AB}_{JI} + a_s^2 c^{BA}_{JI} + a_s^2 c^{AB}_{IJ}\right) \qquad (4.84) \\
&= E\left(a_s^2 c^{AB}_{IJ} - a_s c^{BA}_{IJ}\right) \; . \qquad (4.85)
\end{aligned}$$

It is, of course, noteworthy that the above simplification yields a tensor that is disconnected from the summed indices occurring in the tensor contraction of E. This is a characteristic property of the CI problem. The tensor quantities in the coupled cluster method are always connected to fragments of the hamiltonian via summed indices.

Nevertheless, the discussion from above shows that the term simplification method presented in this work still holds for the simplification of the terms occuring in the configuration interaction ansatz.

4.3.3.4 Summary

In the preceding sections the term simplification derived was discussed using example terms. Several properties of the method could be pointed out.

First of all, the contraction via commutator expressions always yields two terms which, in a diagram, stand for particle-particle and hole-hole contractions, respectively. This is a very instructive picture, since it illustrates that there are always two possibilities to contract two vertices of diagram fragments. This generates two paths in a diagram with anti-parallel directions. This feature could also be interpreted as a kind of particle-hole symmetry of the system considered.

Via the contraction of two vertices a new, extended, vertex is created in a diagram corresponding to a substitution operator that shares all properties with an ordinary vertex.

Thus, vertices and extended vertices can be treated on exactly the same footing.[5]

Finally it should be pointed out that the derived term simplification has a natural resemblance to the step-by-step construction of diagrams. For every pair of vertices one can choose two distinct contraction patterns, namely particle-particle and hole-hole. According to the diagrammatic sign rules these two possibilities generate terms with different sign. The expansion of products mentioned earlier somehow corresponds to the choice of the vertex to be contracted. Impossible contraction patterns vanish in the algebraic formulation due to particle-hole contractions, upper left particle creators or lower right particle annihilators.

[5] Which is exactly what is done for the effective one particle part of the normal ordered hamiltonian. Precontracted parts of the two particle operator are condensed, together with the original one particle part, into the cross in the normal ordered Fock operator diagram.

Chapter 5
Implementation

Contents

5.1 General Considerations

The implementation of the algebraic term simplification has been done in the framework of the *Quantum Objects Library* (QOL), initiated by HANRATH and developed and maintained in the Cologne Quantum Chemistry Group. The QOL program package is written in the C++ language and designed to be as abstract as possible to deal with a vast field of related problems while keeping the numerical evaluation highly efficient.

As a program package it includes many different applications such as an integral routine, a (two-component) HARTREE-FOCK and modules that can perform (multi reference) configuration intraction and coupled cluster calculations for arbitrary excitation levels.

5.1.1 Status Quo

In the QOL program package a mainly statically typed[1] term simplification was included prior to this work. The dynamic part of the term simplification restricted itself to the evaluation of compound operator expressions such as the evaluation of exponentials or powers of operators. This is due to the fact that all (compound) operators involved in the evaluation of coupled cluster type equations, especially including powers of normal ordered operators, can be rewritten in terms of sums of products of second quantized operators. The dynamic term simplification thus, despite being of a rather involved implementational complexity, acted on symbolical operators only.

In the following a short example will be discussed. A common expression in the evaluation of coupled cluster type equations is the power of an operator multiplied by a sum of operators:

$$(\hat{F}_N + \hat{V}_N) \cdot \hat{T}_2^2 \ . \tag{5.1}$$

This expression can be evaluated in a few steps to yield a simple sum of products:

$$\begin{aligned}(\hat{F}_N + \hat{V}_N) \cdot \hat{T}_2^2 &= \hat{F}_N \cdot \hat{T}_2^2 + \hat{V}_N \cdot \hat{T}_2^2 && (5.2)\\ &= \hat{F}_N \cdot \hat{T}_2 \cdot \hat{T}_2 + \hat{V}_N \cdot \hat{T}_2 \cdot \hat{T}_2 \ . && (5.3)\end{aligned}$$

The last line of the preceeding equation can be substituted by products of annihilation and creation operators in order to evaluate the expression employing WICK's second theorem. At this stage the structure of the expressions remains fixed until the evaluation is complete. The expression can always be described by a sum of products of elementary objects, such as tensor quantities, annihilation or creation operators or KRONECKER symbols. Thus the evaluation of WICK's theorem can be depicted by the following workflow:

Consequently the major part of the evaluation of the above expression consists of the manipulation of static objects.

[1] Static in this context has to be understood as an hard coded algorithm without the necessity to identify objects or structures at runtime.

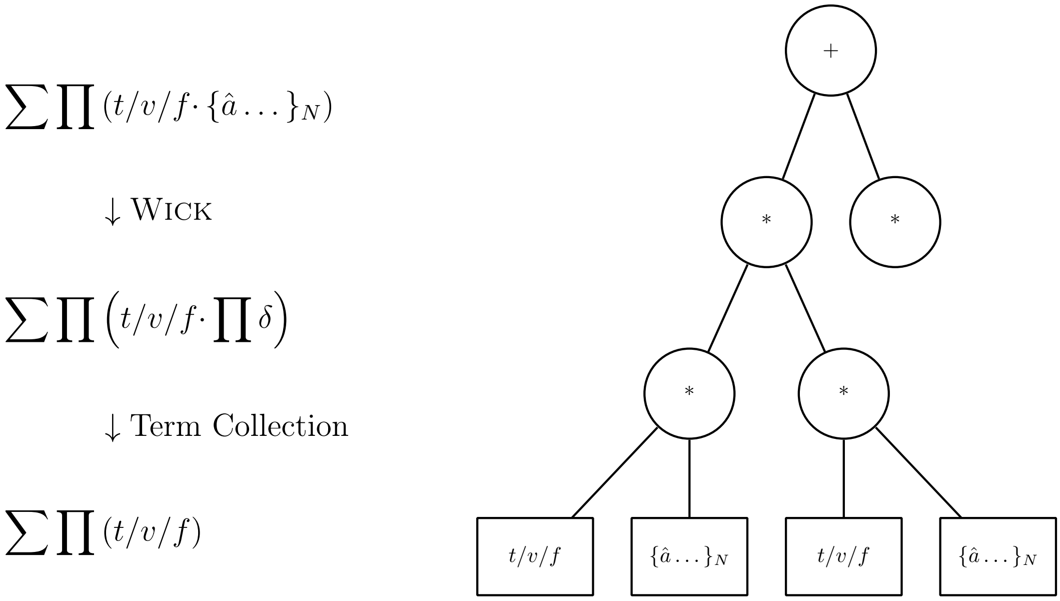


Figure 5.1: Scheme of the static term simplification included in the QOL: (l.h.s.) Workflow diagram for the term simplification employing Wick's theorem and subsequent term collection, (r.h.s.) fixed tree structure of the expressions occuring in the static term simplification. Please note that the expression leafs are of different types during the evaluation. In the tree above only the initial expression is depicted.

The evaluation of static expressions has several advantages, among which are simplicity of as well written and compiled code, speed and readability. Nevertheless a static term simplification is not applicable to the algebraic framework presented in this work.

5.2 Basic Algorithm

The starting point for the algorithm implemented is the result of the evaluation of the Baker-Campbell-Hausdorff expansion of the similarity transformed hamiltonian:

$$\langle\Phi_0|e^{-\hat{E}}\hat{H}e^{\hat{E}}\;\;\Phi_0\rangle = \underbrace{\langle\Phi_0|\hat{H}\;\;\Phi_0\rangle}_{E_{(\mathrm{R})\mathrm{HF}}} + \langle\Phi_0|[\hat{H},\hat{E}]\;\;\Phi_0\rangle + \ldots\ . \tag{5.4}$$

In a normal ordered framework the first term on the right hand side obviously vanishes due to missing contractions.

Subsequently, the products of single substituters contained in the commutator expansion are expressed as a sum over products containing commutators of single substituters only:

$$\langle\Phi_0|[\hat{\sigma}^{qs}_{pr},\hat{\sigma}^{ab}_{ij}]\;\;\Phi_0\rangle = \cdots + \underbrace{\langle\Phi_0|\hat{\sigma}^{a}_{i}[\hat{\sigma}^{q}_{p},\hat{\sigma}^{b}_{j}]\hat{\sigma}^{s}_{r}\;\;\Phi_0\rangle}_{=0} + \langle\Phi_0|\hat{\sigma}^{q}_{p}[\hat{\sigma}^{s}_{r},\hat{\sigma}^{a}_{i}]\hat{\sigma}^{b}_{j}\;\;\Phi_0\rangle + \ldots\ . \tag{5.5}$$

During the further evaluation, the commutator expressions are reduced to contractions and single substitution operators:

$$\langle\Phi_0|\hat{\sigma}_p^q[\hat{\sigma}_r^s,\hat{\sigma}_i^a]\hat{\sigma}_j^b\ \ \Phi_0\rangle = \delta_{ra}\langle\Phi_0|\hat{\sigma}_p^q\hat{\sigma}_i^s\hat{\sigma}_j^b\ \ \Phi_0\rangle - \delta_{is}\langle\Phi_0|\hat{\sigma}_p^q\hat{\sigma}_r^a\hat{\sigma}_j^b\ \ \Phi_0\rangle\ . \tag{5.6}$$

This step of the term simplification is done recursively (corresponding to the innermost loop in listing 5.1). The innermost commutator expression is evaluated followed by an expansion of the commutator exploiting bi-linearity. If the resulting expression still contains commutators of single substituters the procedure is applied again.

After the expression does not change anymore, a series of new commutators is generated if possible:

$$\delta_{is}\langle\Phi_0|\hat{\sigma}_p^q\hat{\sigma}_r^a\hat{\sigma}_j^b\ \ \Phi_0\rangle = \delta_{is}\langle\Phi_0|[[\hat{\sigma}_p^q,\hat{\sigma}_r^a],\hat{\sigma}_j^b]\ \ \Phi_0\rangle\ . \tag{5.7}$$

Due to the fact that all possible new commutator relations can be generated at once this procedure is called only once in every loop. Still it has to be distinguished between the generation of projection commutators (involving operators with lower particle annihilators) and excitation commutators (involving operators with upper particle creators). This is a crucial point in commutator generation because the simultaneous generation of both types of commutators is not canonical, e.g.:

$$\begin{aligned}\hat{\sigma}_A^I\hat{\sigma}_p^q\hat{\sigma}_i^a &= [\hat{\sigma}_A^I,\hat{\sigma}_p^q\hat{\sigma}_i^a] &\quad (5.8)\\ &= [\hat{\sigma}_A^I\hat{\sigma}_p^q,\hat{\sigma}_i^a]\ . &\quad (5.9)\end{aligned}$$

Although the result is not affected by this phenomenon, it is inconvenient to include arbitrary orderings into the algorithm. As it is sufficient to first evaluate all possible projection contractions and then all possible excitation contractions, the switch in the predicate passed to the commutator generation is done only once.

At this step, the algorithm returns to the commutator reduction according to eq. 5.6 again, until the resulting expression is stationary.

The final step of the algorithm consists of the translation of the fully reduced expression into a sum of tensor symbols. Herein, the remaining single substitution operators are contracted via WICK's theorem (with pre-factors according to spin integration):

$$\begin{aligned} &\langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}\ \ \Phi_0\rangle \leftarrow \frac{1}{4}\sum_{\tilde{i}\tilde{j}\tilde{a}\tilde{b}} v_{\tilde{i}\tilde{j}}^{\tilde{a}\tilde{b}} t_{\tilde{i}\tilde{j}}^{\tilde{a}\tilde{b}} \quad \Big|\ \text{spin orbitals} &\quad (5.10)\\ \text{or}\quad &\langle\Phi_0|e^{-\hat{E}}\hat{H}e^{\hat{E}}\ \ \Phi_0\rangle \leftarrow \sum_{ijab} v_{ij}^{ab} t_{ij}^{ab} \quad \Big|\ \text{spatial orbitals} &\quad (5.11)\end{aligned}$$

The spin integration factor can be easily derived to be one in the spin orbital picture and $2^{n_{\mathrm{op}}}$ in the spin free case, with n_{op} being the number of remaining single substituters.

Listing 5.1: Algorithm for the term simplification. Please note that technical details have been transferred to pseudo-code for convenience.

```

int main() {

string input;
cin >> input;

Expression expr(input);
expr.expand();

Expression.expandHigherOrderOperators();
expr.expand();

    for (bool projection=true,false)
    {
        do {
                do {
                        expr.expandSingleCommutators();
                        expr.expand();
                    }
                while (expr changed);

                expr.generateNewCommutators(projection);
                expr.expand();
            }
        while (expr changed);
    }

TensorSymbolsSum tss(expr);

cout << tss << endl;
}
```

The algorithm presented in listing 5.1 in a rather crude way is the starting point for the design of the implementation.

During every call of the subroutines, e.g. expand(), the nature of the Expression passed is evaluated. In most cases an ExpressionLeaf is returned, which invokes a rather easy handling. If the position of the ExpressionLeaf is in the beginning or the end of an operator string, it is checked if it can be dynamic_casted into a single substitution operator. After that it is evaluated if one of the indices cre() or ann() leads to a vanishing Fermi vacuum expectation value.

For the case of ExpressionList or ExpressionListCommutator an iteration over the components is invoked.

5.3 Design Concepts and Realization

This section will mainly consist of a description of the dynamic expression handling in the QOL. The dynamic part of the code is also used in the spin orbital based implemention prior to this work, where it only applies to the evaluation of arbitrary expressions of the compound operators and not to the actual contraction part.

5.3.1 Polymorphism

The concept of polymorphism describes the implementation of an abstract data structure from which several subtypes are derived. The abstract data type often is represented by a class containing virtual functions that are specified for each subtype individually.

While it is often not needed to actually instantiate an object of the base class type, it is very useful to operate with pointers to the base class, as on dereferencing of the pointer the true data type (i.e. an instantiation of a subclass object) is returned.

Given the case that a pointer to the base class is constructed from a pointer to a subclass, the polymorphic structure still allows the call of a member function that is virtual in the base class and the action descibed in the subclass' definition is invoked.

The above mentioned properties lead to the ability to only specify the actual data type in a dereferencing step. Due to this many parts of the program code can be written in an abstract way not knowing the actual data type. This of course leads to much more compact source code and a huge amount of flexibility.

It is for example possible to expand the class structure by another subtype of the abstract base class without any changes in the part of the code that deals with the actual evaluation.

5.3.2 Expression Handling

There are two classes derived from the base class `ExpressionBase`, namely `ExpressionList` and `ExpressionLeaf` (see fig. 5.2). The first one of these classes is designed to contain sums or products of algebraic expressions[2] while the latter one contains only terms that can or should not be evaluated further in a dynamic manner.

There are several crucial member functions included in these two classes (and of course the base class `ExpressionBase` as `virtual` member functions). These member functions which are named `expand()`, `sortProducts()`, and `collect()` are discussed in detail below.

However, it should be mentioned for convenience that `ExpressionLists` split up into two types. These are namely `ExpressionList::Product` and `ExpressionList::Sum`. It is noteworthy that the addition of objects is always considered to be commutative and thus usually instantiated by a type derived from `std::map<Field, Object>` while products have an intrinsic order (due to possible non commutative behavior) and are consequently

[2] Which by themselves can contain sums or products.

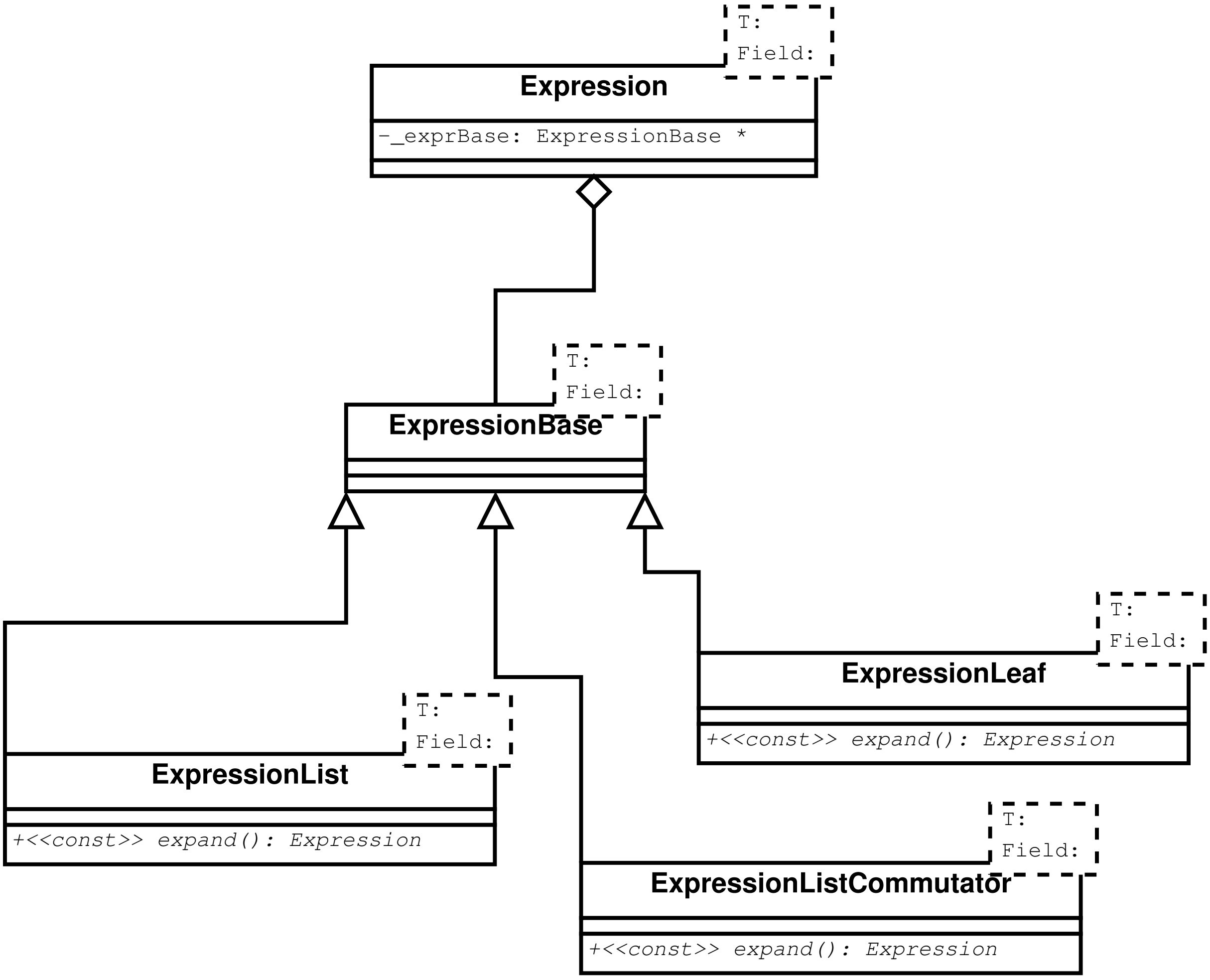

T:
Field:
Expression
-_exprBase: ExpressionBase *
T:
Field:
ExpressionBase
T:
Field:
ExpressionLeaf
+<<const>> expand(): Expression
T:
Field:
ExpressionList
+<<const>> expand(): Expression
T:
Field:
ExpressionListCommutator
+<<const>> expand(): Expression

Figure 5.2: UML class diagram for the dynamic expression handling as used in this work.

constructed as derived classes of `std::vector<Object>`. This leads to the necessity of a `sortProducts()` command in case of commuting objects. For the case of non commuting objects the `sortProducts()` command reduces to a `return *this` statement.

5.3.2.1 The `expand()` Command

The `expand()` command is the most complex one of the member functions of the `Expression` class. This is mainly due to its recursive structure. It makes excessive use of the shared aggregated structure of the dynamic term simplification. Obviously for an `Expression` of type `Expression_Leaf` an expansion is unnecessary. The `expand()` command returns a pointer to `ExpressionBase` instead. The more interesting case is the evaluation of objects of `ExpressionList` type.

Here a subdivision of sum and product objects is needed as a first step. After this product like objects have to be distributed among the addends of the occurring summed objects corresponding to the distributive law. Since both of these object types can possibly consist of objects of both types the evaluation has to be recursive. This procedure ensures the evaluation of low level sums and products before evaluating the higher level terms. As a short example the expansion of the following expression in the (commuting and distributive) variables a, b and c will be given:

$$ac^2 + (ca + b) \cdot c \quad \overset{\texttt{expand()}}{\longrightarrow} \quad ac^2 + cac + bc \,. \tag{5.12}$$

5.3.2.2 The `sortProducts()` Command

It is convenient for commuting objects to sort any expression in a lexicographical order. In order to achieve this first of all a commuting table for any object involved is constructed. These commuting tables are `static` and type specific objects and thus created for all object types possibly involved in the evaluation of an expression while compiling. The commuting tables will be dealt with in the introduction of the object types necessary for this work.

The `expand()` command, as mentioned above, is constructed in a recursive manner which allows a call of `sortProducts()` at every level of the expression evaluation. Thus the `sortProducts()` function is simpler in construction since any expression passed to it is already fully expanded into basic objects (i.e. sums of products of `ExpressionLeafs`).

Since the `sortProducts()` function mainly consists of a call of `std::sort()` a simple example of its action on the result of eq. 5.12 should suffice:

$$ac^2 + cac + bc \quad \overset{\texttt{sortProducts()}}{\longrightarrow} \quad ac^2 + acc + bc \,. \tag{5.13}$$

5.3.2.3 The `collect()` Command

The collection of terms in a sum is in principle straightforward and is dealt with via the `std::map<Field, Object>` structure of sums. Due to this the main task of the `collect()` command is the symbolic conversion of adjacent equal objects in products to a power representation. An example of the action of the `collect()` command is given below:

$$ac^2 + acc + bc \quad \overset{\texttt{collect()}}{\longrightarrow} \quad 2ac^2 + bc \,. \tag{5.14}$$

5.3.3 The `ExpressionListCommutator` Class

Commutator expressions in general do not only lack commutativity but also associativity. Keeping this fact in mind it is clear that this kind of expression cannot be represented in the spirit of `ExpressionList` and needs a seperate class.

Thus the task of implementing commutators into the existing QOL structure is the generation of a new object type `ExpressionListCommutator` that behaves distributive, non-commutative and non-associative, e.g. in general it is:

$$A[B,C] \neq [A,B]C \; . \tag{5.15}$$

Thus a canonical form of writing commutator expressions has to be agreed on. The two problems mentioned above will in the following be discussed with respect to the design of the class `ExpressionListCommutator` which is derived from `ExpressionBase` (as can be seen in fig. 5.2) and `std::list<Object>`. The derivation of the new class from `ExpressionBase` is mainly due to technical considerations. The dynamic framework discussed so far is of an implementational complexity that guarantees absolute flexibility in the expressions inserted to it, meaning that a completely new design of the framework would lead to a loss of this flexibility for the tasks that are already performed in this framework (e.g. generation of coupled cluster working equations, evaluation of powers of the hamiltonian).

As already mentioned above the `ExpressionListCommutator` class is publicly derived from the standard template library (STL) class `std::list<Object>`. This design allows to make extensive use of the `std::list<Object>` member functions `push_back(Object o)`, `insert(Object o, iterator i)`, `erase(iterator i)` and `clear()` for the extension, manipulation and deletion of commutator expressions.

Additionally the `std::list<Object>` structure resembles the tree like structure of the expressions involved in a natural way. For example the `insert(Object o, iterator i)` command is capable of inserting a whole sublist into the original list while operating on the iterator structure of `std::list<Object>` only and thus avoiding time consuming copy operations.

Furthermore the `size()` command can be expoited for a fast identification of non-equal expressions.

A similar design pattern has already been implemented for the `ExpressionList` subtype. Please note that for this type (subdivided into sums and products) the usage of associativity makes the representation even more powerful.

Nevertheless the previously described classes only provide the algorithmic backbone of the term simplification. The task of filling the abstract classes with actual data structures resembling second quantized operators has still to be discussed.

5.3.3.1 Tree Structures

In the last section the focus laid on the structure of the individual commands implemented in the `Expression` class as member functions. However, their real power is only visible when combined. A glance of the work-flow of these member functions has been given with the simple example considered above. A real example of course consists of several nested objects of the above mentioned types. The key design concept becomes visible only for a more involved example like the following one:

$$ab(c+de)+ced(a+bc) = \underbrace{\underbrace{\underbrace{ab}_{\text{level 2}}\;\underbrace{(c+\underbrace{de}_{\text{level 3}})}_{\text{level 2}}}_{\text{level 1}} + \underbrace{\underbrace{ced}_{\text{level 2}}\;\underbrace{(a+\underbrace{bc}_{\text{level 3}})}_{\text{level 2}}}_{\text{level 1}}}_{\text{level 0}} \ . \tag{5.16}$$

The call of `expand()` recognizes a sum as the uppermost level ('level 0') and recursively calls itself on the products contained ('level 1'). The first action of the term simplification starts at 'level 2' where `sortProducts()` rearranges the term *ced* to *cde* in case of given commutativity. As nothing has to be evaluated and/or sorted within the brackets on 'level 2', `expand()` applies the distributive law yielding:

$$ab(c+de)+ced(a+bc) = abc + abde + ceda + cedbc \ . \tag{5.17}$$

Since multiplication of a term with another one is defined as an inplace operation the terms of eq. 5.17 are now the components of `ExpressionList` and thus sorted:

$$ab(c+de)+ced(a+bc) = abc + abde + acde + bccde \ . \tag{5.18}$$

At this stage of simplification `collect()` ensures the power representation of the last term. The term simplification finishes with the following result:

$$ab(c+de)+ced(a+bc) = abc + abde + acde + bc^2de \ . \tag{5.19}$$

5.3.3.2 Algebraic Term Simplification

For the handling of arbitrarily nested expressions a tree like structure as in Fig. 5.3 is considered. For this example the algebraic term is given by:

$$[[A, B\cdot C], D] \ . \tag{5.20}$$

After expansion of this term a sum of four products of nested commutators is gained (cf. eq. 5.21 and fig. 5.4):

$$[[A, B], D]\cdot C + [A, B]\cdot[C, D] + [B, D]\cdot[A, C] + B\cdot[[A, C], D] \ . \tag{5.21}$$

Once the operator expression is in the shape of eq. 5.21 the nested commutator expressions can be replaced by their contracted versions, e.g.:

$$[\hat{\sigma}_p^q, \hat{\sigma}_r^s] = \delta_{ps}\hat{\sigma}_r^q - \delta_{rq}\hat{\sigma}_p^s \ . \tag{5.22}$$

Now the expression does not contain any commutator parts any more, therefore new commutator relations have to be sought. This is done by replacing suited product terms by their commutator analogues as in

$$\hat{\sigma}_i^p\hat{\sigma}_q^a = [\hat{\sigma}_i^p, \hat{\sigma}_q^a] \ . \tag{5.23}$$

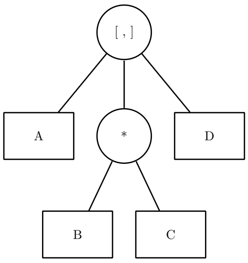


Figure 5.3: Tree representation of a nested expression before simplification.

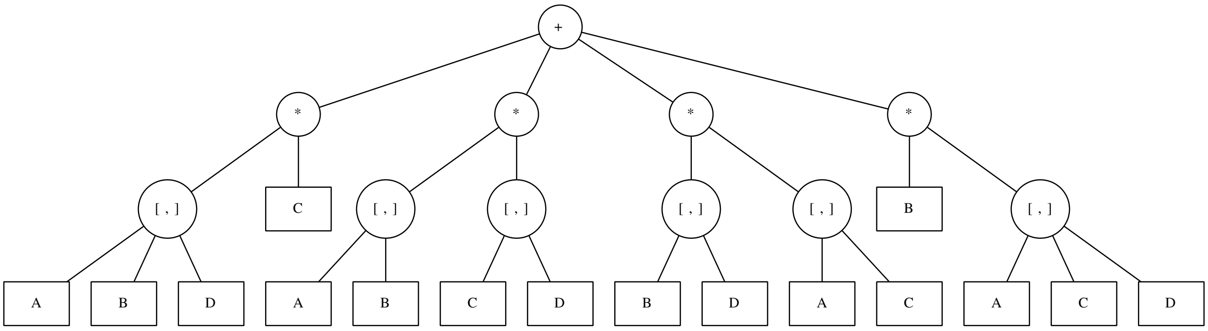


Figure 5.4: Tree representation of a nested expression after simplification.

5.3.4 Polymorphism Implementation

In order to actually fill the abstract evaluation algorithm with data types a polymorphic inheritance scheme was employed. The structure of this implementation is discussed in the following (cf. also fig. 5.5).

In the term simplification program the concept of subtype polymorphism has been implemented in a two step procedure. First of all, the actual data types `SISingleSubstituter`, `SISubstituter` and `Kronecker` give rise to inherited classes that are also subclasses of an abstract class called `SQPolymorphPrimitive`.

The class `SQPolymorphPrimitive` is again derived from `CompoundOperator::Polymorph` which is a member class of `CompoundOperator`. The latter is the actual specification of the template used in the expression evaluation.

The algebraic evaluation takes place employing the `CompoundOperator_Expression` which binds the templates `T` and `Field` to the types `CompoundOperator` and `RationalNumber`, respectively. This means that the abstract algorithm discussed before (see sec. 5.3.2) is now applied to an object holding a pointer to `CompoundOperator::Polymorph`, which can be dereferced to yield any of the actual data types.

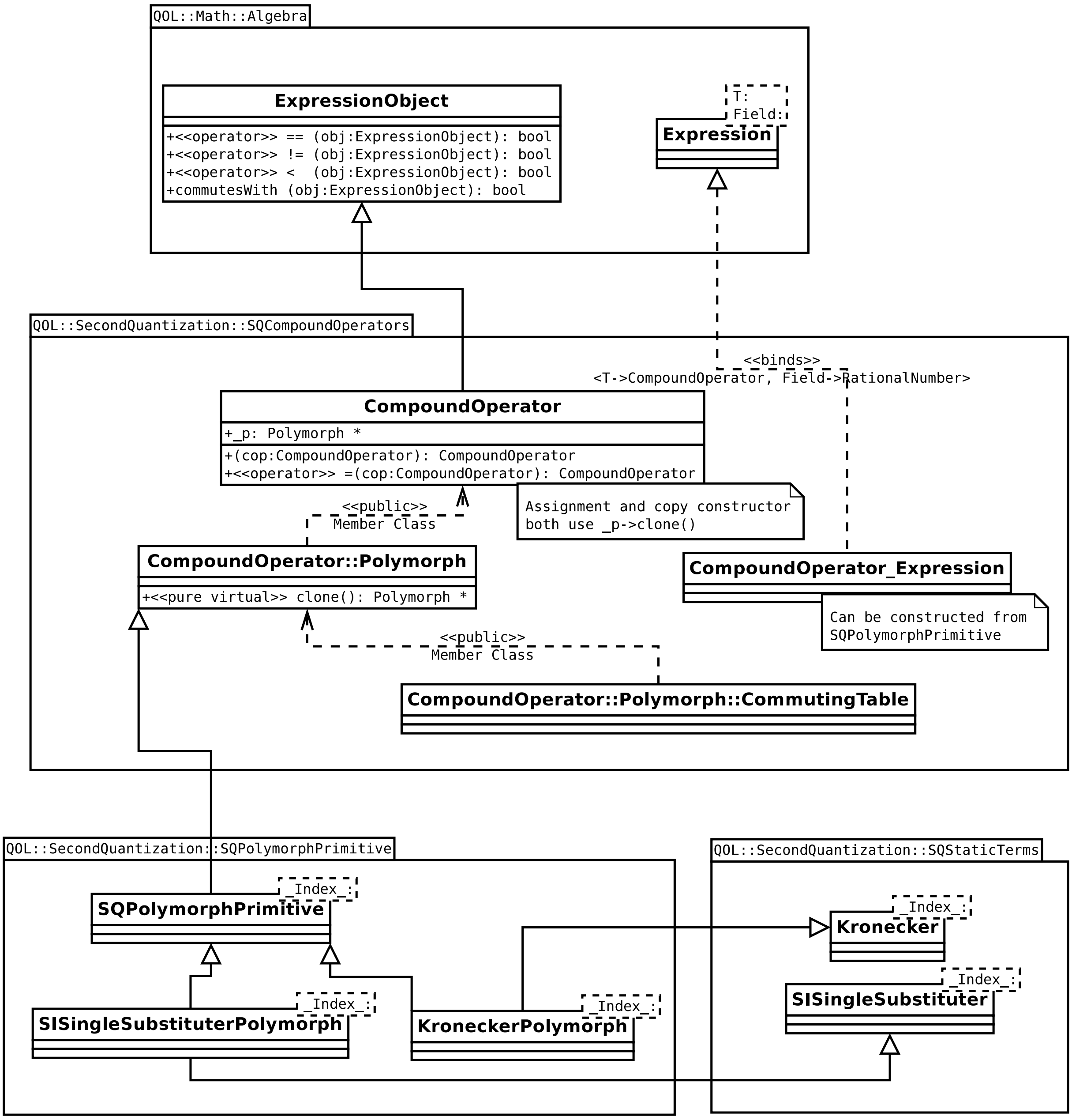

QOL::Math::Algebra
ExpressionObject
+<<operator>> == (obj:ExpressionObject): bool
+<<operator>> != (obj:ExpressionObject): bool
+<<operator>> < (obj:ExpressionObject): bool
+commutesWith (obj:ExpressionObject): bool
T:
Field:
Expression
QOL::SecondQuantization::SQCompoundOperators
<<binds>>
<T->CompoundOperator, Field->RationalNumber>
CompoundOperator
+_p: Polymorph *
+(cop:CompoundOperator): CompoundOperator
+<<operator>> =(cop:CompoundOperator): CompoundOperator
Assignment and copy constructor
both use _p->clone()
<<public>>
Member Class
CompoundOperator::Polymorph
+<<pure virtual>> clone(): Polymorph *
CompoundOperator_Expression
Can be constructed from
SQPolymorphPrimitive
<<public>>
Member Class
CompoundOperator::Polymorph::CommutingTable
QOL::SecondQuantization::SQPolymorphPrimitive
Index:
SQPolymorphPrimitive
Index:
SISingleSubstituterPolymorph
Index:
KroneckerPolymorph
QOL::SecondQuantization::SQStaticTerms
Index:
Kronecker
Index:
SISingleSubstituter

Figure 5.5: UML class diagram for the main dependencies in the dynamic term simplification.

5.4 Input and Output Syntax

5.4.1 Syntax for Compound Operator Expressions

The input of compound operator expressions was only modified marginally. For products and sums of expressions an intuitive syntax has already been implemented as follows:

$$\langle \Phi_0 | (\hat{F}_N + \hat{V}_N) \cdot \hat{T}_2 \; \Phi_0 \rangle \equiv \texttt{expr(FV((FN+VN)*T(2)))}. \tag{5.24}$$

The acronym FV in eq. 5.24 resembles the Fermi vacuum expectation value.

5.4.1.1 Canonical Syntax for Commutator Expressions

The arbitrariness in the depiction of commutator expressions due to their lack of associativity was already discussed above. For implementational purposes a left aligned nested commutator order was chosen. This has to be understood as follows:

$$\langle \Phi_0 | [[[\hat{V}_N, \hat{T}_1], \hat{T}_1], \hat{T}_1] \; \Phi_0 \rangle \equiv \texttt{expr(FV(VN|T(1)|T(1)|T(1)))}. \tag{5.25}$$

Please note that the usage of the "|" operator overrides the definition of the binary "or" relation.

5.4.2 Output Syntax

For the output procedure two variants have been implemented. First of all there is a standard XML output operator, which is compatible with the QOL's own XML to LaTeX converter. Every sample output discussed below was given in the concatenated manner of XML. Additionally for every type involved in the term simplification a seperate XML tag has been written alongside a XML to LaTeX translation.

In a similar fashion the GraphViz, or dot, output has been designed. Every class involved in the dynamic term simplification includes its own output type for the GraphViz's dot2tex routine. According to this design tree like structures (as in figs. 5.3 and 5.4) can be visualized, although due to the term complexity mainly for debugging purposes.

5.4.2.1 Example Program Outputs

In order to show the work flow of the term simplification implemented two example program outputs are given below. The outputs are similar in terms of evaluating the same symbolic operator expression. Facing this example, one can see that there is no increase in complexity for spin independent expressions in this type of term simplification.

As a first example the evaluation of the symbolic operator expression

$$R_{\tilde{I}}^{\tilde{A}} \qquad \longleftarrow \qquad \left\langle \Phi_0 \middle| \hat{\tau}_{\tilde{A}}^{\tilde{I}} [\hat{\tau}_{\tilde{p}}^{\tilde{q}}, \hat{\tau}_{\tilde{i}\tilde{j}}^{\tilde{a}\tilde{b}}] \;\; \Phi_0 \right\rangle \tag{5.26}$$

Initial Input:

$\hat{\tau}^I_A[\hat{\tau}^q_p, \hat{\tau}^{ab}_{ij}]$

Expanded:

$\hat{\tau}^I_A[\hat{\tau}^q_p, \hat{\tau}^a_i]\hat{\tau}^b_j + \hat{\tau}^I_A\hat{\tau}^a_i[\hat{\tau}^q_p, \hat{\tau}^b_j]$

Cycle: 0, Single Commutators expanded:

$\delta_{ap}\hat{\tau}^I_A\hat{\tau}^q_i\hat{\tau}^b_j + \delta_{bp}\hat{\tau}^I_A\hat{\tau}^a_i\hat{\tau}^q_j - \delta_{qi}\hat{\tau}^I_A\hat{\tau}^a_p\hat{\tau}^b_j - \delta_{qj}\hat{\tau}^I_A\hat{\tau}^a_i\hat{\tau}^b_p$

Cycle: 0, New Commutators generated:

$-\delta_{ap}\hat{\tau}^q_i[\hat{\tau}^b_j, \hat{\tau}^I_A] - \delta_{ap}[\hat{\tau}^q_i, \hat{\tau}^I_A]\hat{\tau}^b_j - \delta_{bp}\hat{\tau}^a_i[\hat{\tau}^q_j, \hat{\tau}^I_A] - \delta_{bp}[\hat{\tau}^a_i, \hat{\tau}^I_A]\hat{\tau}^q_j + \delta_{qi}\hat{\tau}^a_p[\hat{\tau}^b_j, \hat{\tau}^I_A] + \delta_{qi}[\hat{\tau}^a_p, \hat{\tau}^I_A]\hat{\tau}^b_j + \delta_{qj}\hat{\tau}^a_i[\hat{\tau}^b_p, \hat{\tau}^I_A] + \delta_{qj}[\hat{\tau}^a_i, \hat{\tau}^I_A]\hat{\tau}^b_p$

Cycle: 1, Single Commutators expanded:

$-\delta_{Ii}\delta_{ap}\hat{\tau}^q_A\hat{\tau}^b_j - \delta_{Ii}\delta_{bp}\hat{\tau}^a_A\hat{\tau}^q_j + \delta_{Ii}\delta_{qj}\hat{\tau}^a_A\hat{\tau}^b_p - \delta_{Ij}\delta_{ap}\hat{\tau}^q_i\hat{\tau}^b_A - \delta_{Ij}\delta_{bp}\hat{\tau}^a_i\hat{\tau}^q_A + \delta_{Ij}\delta_{qi}\hat{\tau}^a_p\hat{\tau}^b_A + \delta_{Ip}\delta_{qi}\hat{\tau}^a_A\hat{\tau}^b_j + \delta_{Ip}\delta_{qj}\hat{\tau}^a_i\hat{\tau}^b_A + \delta_{aA}\delta_{bp}\hat{\tau}^I_i\hat{\tau}^q_j - \delta_{aA}\delta_{qi}\hat{\tau}^I_p\hat{\tau}^b_j - \delta_{aA}\delta_{qj}\hat{\tau}^I_i\hat{\tau}^b_p + \delta_{ap}\delta_{bA}\hat{\tau}^q_i\hat{\tau}^I_j + \delta_{ap}\delta_{qA}\hat{\tau}^I_i\hat{\tau}^b_j - \delta_{bA}\delta_{qi}\hat{\tau}^a_p\hat{\tau}^I_j - \delta_{bA}\delta_{qj}\hat{\tau}^a_i\hat{\tau}^I_p + \delta_{bp}\delta_{qA}\hat{\tau}^a_i\hat{\tau}^I_j$

Cycle: 1, New Commutators generated:

$-\delta_{Ii}\delta_{ap}[\hat{\tau}^q_A, \hat{\tau}^b_j] - \delta_{Ij}\delta_{ap}[\hat{\tau}^q_i, \hat{\tau}^b_A] - \delta_{aA}\delta_{qi}[\hat{\tau}^I_p, \hat{\tau}^b_j] - \delta_{aA}\delta_{qj}[\hat{\tau}^I_i, \hat{\tau}^b_p] + \delta_{ap}\delta_{qA}[\hat{\tau}^I_i, \hat{\tau}^b_j] + \delta_{aA}\delta_{bp}\hat{\tau}^I_i\hat{\tau}^q_j + \delta_{ap}\delta_{bA}\hat{\tau}^q_i\hat{\tau}^I_j$

Cycle: 2, Single Commutators expanded:

$-\delta_{Ii}\delta_{ap}\delta_{bA}\hat{\tau}^q_j + \delta_{Ii}\delta_{ap}\delta_{qj}\hat{\tau}^b_A + \delta_{Ij}\delta_{aA}\delta_{qi}\hat{\tau}^b_p + \delta_{Ip}\delta_{aA}\delta_{qj}\hat{\tau}^b_i - \delta_{aA}\delta_{bp}\delta_{qi}\hat{\tau}^I_j + \delta_{aA}\delta_{bp}\hat{\tau}^I_i\hat{\tau}^q_j + \delta_{ap}\delta_{bA}\hat{\tau}^q_i\hat{\tau}^I_j$

Cycle: 2, New Commutators generated:

$-\delta_{Ii}\delta_{ap}\delta_{bA}\hat{\tau}^q_j - \delta_{aA}\delta_{bp}\delta_{qi}\hat{\tau}^I_j + \delta_{aA}\delta_{bp}\hat{\tau}^I_i\hat{\tau}^q_j + \delta_{ap}\delta_{bA}\hat{\tau}^q_i\hat{\tau}^I_j$

Final Result:

$-\delta_{Ii}\delta_{jq}\delta_{ap}\delta_{bA} + \delta_{iI}\delta_{jq}\delta_{aA}\delta_{bp} + \delta_{iq}\delta_{jI}\delta_{ap}\delta_{bA} - \delta_{jI}\delta_{aA}\delta_{bp}\delta_{qi} \quad (= 2f^a_i t^{Aa}_{Ii} - 2f^a_i t^{aA}_{Ii})$

Figure 5.6: Program Output for spin orbitals.

is considered in the spin orbital framework (cf. fig. 5.6). The individual generation and evaluation steps are included in order to easily follow the evaluation.

It should be noted that the very last step (the condensation of the Kronecker symbols into a tensor contraction) was done by hand. In principle the presented program is capable of the transformation involved in this step, as long as tensor symmetries are nor considered. Thus, the presented program would have generated four individual terms, two of which are related by simultaneous permutation of upper and lower indices, respectively.

Exactly the same simplifiction has been applied to the spin independent operator expression

$$R_I^A \qquad \longleftarrow \qquad \left\langle \Phi_0 \left| \hat{\eta}^I_A [\hat{\eta}^q_p, \hat{\eta}^{ab}_{ij}] \;\; \Phi_0 \right.\right\rangle \; . \tag{5.27}$$

As can be seen from fig. 5.7, the evaluation steps do not differ from the spin orbital based evaluation. Only the very last step[3] differs from the spin orbital evaluation presented in the preceding figure.

5.5 The SICluster Term Simplification Program

After the discussion of the implementational details of the expression handling and the polymorphic design of the data structures the focus will now lie on the actual term simplification program already introduced schematically in listing 5.1.

The linear program design of listing 5.1 has been hidden in nested function calls in the actual implementation. This has been done for reasons of clarity and readability. The main function can be written as simple as:

```
1 int main() {
2
3 LastUsedSQIndex lui, lui2;
4 CompoundOperator_Expression coexpr(D(2,lui2)*(V(lui2)|E(2,lui)|E(2,lui))
    );
5 TensorSymbols_Sum<SQIndex, false> tss;
6
7   Expr2tss(coexpr, tss);
8 cout << tss << endl;
9 }
```

In lines three to five the necessary objects are constructed, where the `LastUsedSQIndex` variables are used for index naming purposes only. The actual term simplification is called in line seven.

[3] Also done by hand in this case, but implemented to be done automatically. The only difference to the presented result is the occurance of four terms since tensor symmetry upon simultaneous permutation of annihilator and creator indices is not implemented.

Initial Input:

$\hat{\eta}^{I}_{A}[\hat{\eta}^{q}_{p},\hat{\eta}^{ab}_{ij}]$

Expanded:

$\hat{\eta}^{I}_{A}[\hat{\eta}^{q}_{p},\hat{\eta}^{a}_{i}]\hat{\eta}^{b}_{j}+\hat{\eta}^{I}_{A}\hat{\eta}^{a}_{i}[\hat{\eta}^{q}_{p},\hat{\eta}^{b}_{j}]$

Cycle: 0, Single Commutators expanded:

$\delta_{ap}\hat{\eta}^{I}_{A}\hat{\eta}^{q}_{i}\hat{\eta}^{b}_{j}+\delta_{bp}\hat{\eta}^{I}_{A}\hat{\eta}^{a}_{i}\hat{\eta}^{q}_{j}-\delta_{qi}\hat{\eta}^{I}_{A}\hat{\eta}^{a}_{p}\hat{\eta}^{b}_{j}-\delta_{qj}\hat{\eta}^{I}_{A}\hat{\eta}^{a}_{i}\hat{\eta}^{b}_{p}$

Cycle: 0, New Commutators generated:

$-\delta_{ap}\hat{\eta}^{q}_{i}[\hat{\eta}^{b}_{j},\hat{\eta}^{I}_{A}]-\delta_{ap}[\hat{\eta}^{q}_{i},\hat{\eta}^{I}_{A}]\hat{\eta}^{b}_{j}-\delta_{bp}\hat{\eta}^{a}_{i}[\hat{\eta}^{q}_{j},\hat{\eta}^{I}_{A}]-\delta_{bp}[\hat{\eta}^{a}_{i},\hat{\eta}^{I}_{A}]\hat{\eta}^{q}_{j}+\delta_{qi}\hat{\eta}^{a}_{p}[\hat{\eta}^{b}_{j},\hat{\eta}^{I}_{A}]+\delta_{qi}[\hat{\eta}^{a}_{p},\hat{\eta}^{I}_{A}]\hat{\eta}^{b}_{j}+$
$\delta_{qj}\hat{\eta}^{a}_{i}[\hat{\eta}^{b}_{p},\hat{\eta}^{I}_{A}]+\delta_{qj}[\hat{\eta}^{a}_{i},\hat{\eta}^{I}_{A}]\hat{\eta}^{b}_{p}$

Cycle: 1, Single Commutators expanded:

$-\delta_{Ii}\delta_{ap}\hat{\eta}^{q}_{A}\hat{\eta}^{b}_{j}-\delta_{Ii}\delta_{bp}\hat{\eta}^{a}_{A}\hat{\eta}^{q}_{j}+\delta_{Ii}\delta_{qj}\hat{\eta}^{a}_{A}\hat{\eta}^{b}_{p}-\delta_{Ij}\delta_{ap}\hat{\eta}^{q}_{i}\hat{\eta}^{b}_{A}-\delta_{Ij}\delta_{bp}\hat{\eta}^{a}_{i}\hat{\eta}^{q}_{A}+\delta_{Ij}\delta_{qi}\hat{\eta}^{a}_{p}\hat{\eta}^{b}_{A}+\delta_{Ip}\delta_{qi}\hat{\eta}^{a}_{A}\hat{\eta}^{b}_{j}+$
$\delta_{Ip}\delta_{qj}\hat{\eta}^{a}_{i}\hat{\eta}^{b}_{A}+\delta_{aA}\delta_{bp}\hat{\eta}^{I}_{i}\hat{\eta}^{q}_{j}-\delta_{aA}\delta_{qi}\hat{\eta}^{I}_{p}\hat{\eta}^{b}_{j}-\delta_{aA}\delta_{qj}\hat{\eta}^{I}_{i}\hat{\eta}^{b}_{p}+\delta_{ap}\delta_{bA}\hat{\eta}^{q}_{i}\hat{\eta}^{I}_{j}+\delta_{ap}\delta_{qA}\hat{\eta}^{I}_{i}\hat{\eta}^{b}_{j}-\delta_{bA}\delta_{qi}\hat{\eta}^{a}_{p}\hat{\eta}^{I}_{j}-$
$\delta_{bA}\delta_{qj}\hat{\eta}^{a}_{i}\hat{\eta}^{I}_{p}+\delta_{bp}\delta_{qA}\hat{\eta}^{a}_{i}\hat{\eta}^{I}_{j}$

Cycle: 1, New Commutators generated:

$-\delta_{Ii}\delta_{ap}[\hat{\eta}^{q}_{A},\hat{\eta}^{b}_{j}]-\delta_{Ij}\delta_{ap}[\hat{\eta}^{q}_{i},\hat{\eta}^{b}_{A}]-\delta_{aA}\delta_{qi}[\hat{\eta}^{I}_{p},\hat{\eta}^{b}_{j}]-\delta_{aA}\delta_{qj}[\hat{\eta}^{I}_{i},\hat{\eta}^{b}_{p}]+\delta_{ap}\delta_{qA}[\hat{\eta}^{I}_{i},\hat{\eta}^{b}_{j}]+\delta_{aA}\delta_{bp}\hat{\eta}^{I}_{i}\hat{\eta}^{q}_{j}+$
$\delta_{ap}\delta_{bA}\hat{\eta}^{q}_{i}\hat{\eta}^{I}_{j}$

Cycle: 2, Single Commutators expanded:

$-\delta_{Ii}\delta_{ap}\delta_{bA}\hat{\eta}^{q}_{j}+\delta_{Ii}\delta_{ap}\delta_{qj}\hat{\eta}^{b}_{A}+\delta_{Ij}\delta_{aA}\delta_{qi}\hat{\eta}^{b}_{p}+\delta_{Ip}\delta_{aA}\delta_{qj}\hat{\eta}^{b}_{i}-\delta_{aA}\delta_{bp}\delta_{qi}\hat{\eta}^{I}_{j}+\delta_{aA}\delta_{bp}\hat{\eta}^{I}_{i}\hat{\eta}^{q}_{j}+\delta_{ap}\delta_{bA}\hat{\eta}^{q}_{i}\hat{\eta}^{I}_{j}$

Cycle: 2, New Commutators generated:

$-\delta_{Ii}\delta_{ap}\delta_{bA}\hat{\eta}^{q}_{j}-\delta_{aA}\delta_{bp}\delta_{qi}\hat{\eta}^{I}_{j}+\delta_{aA}\delta_{bp}\hat{\eta}^{I}_{i}\hat{\eta}^{q}_{j}+\delta_{ap}\delta_{bA}\hat{\eta}^{q}_{i}\hat{\eta}^{I}_{j}$

Final Result:

$-\delta_{Ii}\delta_{jq}\delta_{ap}\delta_{bA}+2\delta_{iI}\delta_{jq}\delta_{aA}\delta_{bp}+2\delta_{iq}\delta_{jI}\delta_{ap}\delta_{bA}-\delta_{jI}\delta_{aA}\delta_{bp}\delta_{qi}\quad(=4f^{a}_{i}t^{Aa}_{Ii}-2f^{a}_{i}t^{aA}_{Ii})$

Figure 5.7: Program output for spatial orbitals.

The `Expr2tss` function mainly converts a dynamic expression into the static type `TensorSymbols_Sum<SQIndex, false>`. However, while converting, the function `algebraivEvaluation(CompoundOperator_Expression & coexpr)` is called, as can be seen in the following code snippet:

```
void Expr2tss(CompoundOperator_Expression & coexpr, TensorSymbols_Sum<SQIndex, false> & tss)
{
clean(coexpr);
vector<RationalNumber> prefactors;

    /* gather prefactors */
    {   ... }

    /* gather addends of ExpressionList in std::list of addends */
    {   ...

        if (addends.size()==0)
            tss += prefactors[0]*algebraicEvaluation(coexpr);

        int it=0;
        /* iterate over addends of ExpressionList */
        for ( auto i=addends.begin() ; i!=addends.end() ; ++i, ++it)
        {
            CompoundOperator_Expression expr(**i);
            tss += prefactors[it]*algebraicEvaluation(expr);
        }
    }
}
```

The `algebraicEvaluation(CompoundOperator_Expression & coexpr)` function is the actual place of iteration corresponding to lines 23-35 in the algorithm of listing 5.1. In summary this nesting of functions reduces the code still to be discussed to the functions `evaluateSingleCommutators` and `generateNewCommutators`.

5.5.1 The `evaluateSingleCommutators` Function

In the first step of the evaluation all commutator expressions containing `ExpressionLeafs` as their first two components are gathered in an instance of `list<Expression *>`:

```
void ExpandSingleCommutators(CompoundOperator_Expression & coexpr)
{
coexpr.clean();
/* gather all commutator expressions of leafs in a list */
list<Expression<CompoundOperator, RationalNumber> *>    comms(...);
...
```

This list is the base for the subsequent iteration. Via several statements of the form

```
if (ObjectType * pp = dynamic_cast<ObjectType *>((**comms_iterator).
    exprBase()))
```

it is tested if the objects at position `comms_iterator` and the next one are of type `ExpressionLeaf` and then of type `SISingleSubstituterPolymorph`, which is necessary for their contraction.

If the conditions are fullfilled the nature of the indices contained in the two objects is investigated. For matching indices the return object

```
CompoundOperator_Expression diff=Expression::zero();
```

is updated as follows:

```
1 if (/* [e_p^a,e_i^q] or [e_p^i,e_a^q]*/)
2     diff=CompoundOperator_Expression(kron(p,q)*op({a,i}));
3 else if (/*[e_a^p,e_q^i] or [e_i^p,e_q^a]*/)
4     diff = -CompoundOperator_Expression(kron(p,q)*op({i,a}));
5 else /* [e_p^q,e_r^s]*/
6 {
7     diff =CompoundOperator_Expression(kron(p,s)*op(r,q));
8     diff -= CompoundOperator_Expression(kron(r,q)*op(p,s));
9 }
```

The curly braces in lines two and four have to be read as the suiting index combination. In the actual code, there is another level of differentiation between the two possibiltities occuring in line one and three, respectively.

After this step, the commutator expression has to be brought into canonical form again. This is done by the construction of a new nested commutator of lower order containing `diff` as its first element. The former list element is then replaced by the new commutator expression.

In this fashion all lowest order commutators are evaluated and replaced by their expansion. The iterative call of the `evaluateSingleCommutators` until they yield stable expressions guarantees the full evaluation of all commutators.

5.5.2 The `generateNewCommutators` Function

In order to identify possibilities for a commutator generation, the `generateNewCommutators` function has to run over every factor in every product contained in the expression and check if it is of `ExpressionLeaf` type:

```
1  void GenerateNewCommutators(CompoundOperator_Expression & coexpr, bool
       Projection)
2  {
3
4  /* gather all ExpressionList::Product in a list */
5  list<Expression<CompoundOperator, RationalNumber> *> prods(...);
6
7  /*iterate over list */
8  for ( auto factors=prods.begin() ; factors!=prods.end() ; ++i )
9  {
10     /* iterate over product*/
11     for (auto j=factors->begin(); j!=factors->end(); ++j)
12     {
13         /* check if factor is ExpressionLeaf */
14         if (ExpressionLeaf<CompoundOperator, RationalNumber> * pos=
               dynamic_cast<ExpressionLeaf<CompoundOperator, RationalNumber>
                *>((j->first).exprBase()))
15         {   ...
```

Arriving at line 15, there are two possibilities, either the factor is of `KroneckerPolymorph` or of `SISingleSubstituterPolymorph` type. In the first case not much has to be done. The `KroneckerPolymorph` objects are stored in a product that has to be attached in the end. The latter case is more involved, and again two cases have to be distinguished, depending on the value of the `bool` Projection flag.

For the `Projection==false` case, new commutators are generated for the excitation operators. For this purpose, all non-excitation operators are stored into a product (lines 3-12 in the following code snippet) until the first excitation is identified. Then a new commutator expression is generated out of the product and the excitation operator (lines 13 and 14).

```
1  if (!Projection)
2  {
3      if (v->idxCre().type().isHole())
4      {
5          if (oper_count ==0)
6          {
7              oper_comm =op(v->idxAnn(), v->idxCre());
8              ++oper_count;
9          }
10         else
11             oper_comm *= op(v->idxAnn(), v->idxCre());
12     }
13     else if ((v->idxCre().type().isParticle()) && !(v->idxCre().type().
           isHole())  && oper_count != 0)
14         oper_comm = (oper_comm|(op(v->idxAnn(), v->idxCre())));
15 }
```

Since the iteration runs over all factors a system of nested commutators is generated.

The case of `Projection=true` is similar in many respects. However, since in general the projection operators are located in the front of an operator product, they are gathered in a `std::vector<Expression *>` and the generation of the nested commutator expression is postponed to the end of the iteration:

```
1 if (Projection)
2 {
3 ...
4     for (auto f=oper_dag.begin(); f!=oper_dag.end(); ++f)
5         oper_comm= -(oper_comm| Expression<CompoundOperator,
              RationalNumber>(f->exprBase()->clone()));
6 ...
7 }
```

The minus sign in line five of the above code snippet is due to the canonical order of the commutator expression. Since the projection operators generate new commutators from the left, in each step the commutator has to be explicitly turned around and the resulting sign is attached.

In the end of the commutator generation some vanishing cases are dealt with. The details of these cases are rather technical and are omitted from the discussion.

5.6 Computational Demand

In this section the computational demand of the presented algebraic term simplification will be discussed with respect to the computational demand of a straightforward implementation of Wick's theorem. Despite the recent development and implementation of a fast Wick contraction engine exploiting tensor antisymmetry by Hanrath [96] a comparison with this implementation seems to be a bit unfair. This is due to the special nature of tensor symmetry in the spin independent framework.

5.6.1 Theoretical Considerations

In the following the number of terms occurring at a certain stage of the term simplification will be discussed. There are two main reasons for an increasing number of terms during the algebraic evaluation.

Firstly every commutator of single substitution operators is written as a difference of single substituters multiplied by a Kronecker delta. This leads to a doubling of the number of terms for the evaluation of the innermost commutators after expanding the term via the bi-linearity of the commutator operation. E. g. the nested commutator expression

$$\begin{aligned}
\left\langle \Phi_0 \middle| \left[[\hat{F}_N, \hat{T}_1], \hat{T}_1 \right] \Phi_0 \right\rangle &= \left\langle \Phi_0 \middle| \left[[\hat{\sigma}_p^q, \hat{\sigma}_i^a], \hat{\sigma}_j^b \right] \Phi_0 \right\rangle \qquad (5.28)\\
&= \left\langle \Phi_0 \middle| \left[(\delta_{pa}\hat{\sigma}_i^q - \delta_{iq}\hat{\sigma}_p^a), \hat{\sigma}_j^b \right] \Phi_0 \right\rangle \qquad (5.29)\\
&= \left\langle \Phi_0 \middle| \left[\delta_{pa}\hat{\sigma}_i^q, \hat{\sigma}_j^b \right] \Phi_0 \right\rangle - \left\langle \Phi_0 \middle| \left[\delta_{iq}\hat{\sigma}_p^a, \hat{\sigma}_j^b \right] \Phi_0 \right\rangle \qquad (5.30)
\end{aligned}$$

divides into two terms. Each of these terms itself yields two new terms via

$$\begin{aligned}
\left\langle \Phi_0 \middle| \left[[\hat{F}_N, \hat{T}_1], \hat{T}_1 \right] \Phi_0 \right\rangle &= \delta_{pa}\left\langle \Phi_0 \middle| \left[\hat{\sigma}_i^q, \hat{\sigma}_j^b \right] \Phi_0 \right\rangle - \delta_{iq}\left\langle \Phi_0 \middle| \left[\hat{\sigma}_p^a, \hat{\sigma}_j^b \right] \Phi_0 \right\rangle \qquad (5.31)\\
&= \delta_{pa}\big\langle \Phi_0 \big| \delta_{ib}\hat{\sigma}_j^q - \delta_{jq}\hat{\sigma}_i^b \, \Phi_0 \big\rangle\\
&\quad - \delta_{iq}\big\langle \Phi_0 \big| \delta_{pb}\hat{\sigma}_j^a - \delta_{ja}\hat{\sigma}_i^b \, \Phi_0 \big\rangle \qquad (5.32)\\
&= \delta_{pa}\delta_{ib}\big\langle \Phi_0 \big| \hat{\sigma}_j^q \, \Phi_0 \big\rangle - \delta_{pa}\delta_{jq}\big\langle \Phi_0 \big| \hat{\sigma}_i^b \, \Phi_0 \big\rangle\\
&\quad - \delta_{iq}\delta_{pb}\big\langle \Phi_0 \big| \hat{\sigma}_j^a \, \Phi_0 \big\rangle + \delta_{iq}\delta_{ja}\big\langle \Phi_0 \big| \hat{\sigma}_p^b \, \Phi_0 \big\rangle \; . \qquad (5.33)
\end{aligned}$$

Due to the discussion of this example (and neglecting the fact that several of the above terms vanish due to reasons of non overlapping sets of orbitals and annihilation or creation of unoccupied or occupied orbitals, respectively) it is obvious that the evaluation of nested commutator expressions of single substitution operator generates a total of 2^{n_nest} terms, where n_nest is the depth of the nested commutator.

Secondly every commutator of product expressions is expanded into a sum of products with one factor being a commutator itself. Given the example

$$\left\langle \Phi_0 \middle| [\hat{V}_N, \hat{T}_2] \, \Phi_0 \right\rangle = \left\langle \Phi_0 \middle| [\hat{\sigma}_p^r\hat{\sigma}_q^s, \hat{\sigma}_i^a\hat{\sigma}_j^b] \, \Phi_0 \right\rangle , \qquad (5.34)$$

one can easily obtain the expanded expression

$$\begin{aligned}
\left\langle \Phi_0 \middle| [\hat{V}_N, \hat{T}_2] \, \Phi_0 \right\rangle = \Big\langle \Phi_0 \Big| &\hat{\sigma}_p^r\hat{\sigma}_i^a[\hat{\sigma}_q^s, \hat{\sigma}_j^b] + \hat{\sigma}_p^r[\hat{\sigma}_q^s, \hat{\sigma}_i^a]\hat{\sigma}_j^b\\
&+ \hat{\sigma}_i^a[\hat{\sigma}_p^r, \hat{\sigma}_j^b]\hat{\sigma}_q^s + [\hat{\sigma}_p^r, \hat{\sigma}_i^a]\hat{\sigma}_r^s\hat{\sigma}_j^b \, \Phi_0 \Big\rangle \; . \qquad (5.35)
\end{aligned}$$

In the preceding example it can be seen that a product of two factors inside a simple commutator yields two individual terms involving commutators of single substituters only. In a similar fashion products involving n_prod terms yields exactly n_prod of these terms in the innermost commutator.

It is now interesting to investigate how these two mechanisms of expansion work together. In the implemented algorithm they are designed as function calls following each other. Given an arbitrary expression in the evaluation of nested commutators the expansion of product terms is called first, generating commutator expressions involving single substituters only. When the expansion of these terms is completed, the nested commutators are evaluated. This leads to the fact that the number of terms generated is directly related to the commutator depth via $n = A \cdot 2^{n_{\text{nest}}}$. The pre-factor A is a function of the number of factors involved in each commutator, scaled by the depth the product occurs in. For the investigation of the nature of A the following examples will be considered:

$$\langle \Phi_0 | [(\hat{F}_N + \hat{V}_N), \hat{T}_1] \; \Phi_0 \rangle \,, \tag{ex1}$$

$$\langle \Phi_0 | [[(\hat{F}_N + \hat{V}_N), \hat{T}_1], \hat{T}_1] \; \Phi_0 \rangle \;. \tag{ex2}$$

It is clear that the number of terms in the Fock operator part is given by the commutator depth only, since there are no products of single substituters involved. Thus the discussion will concentrate on the following parts of the example expressions:

$$\langle \Phi_0 | [\hat{V}_N, \hat{T}_1] \; \Phi_0 \rangle \,, \tag{ex1'}$$

$$\langle \Phi_0 | [[\hat{V}_N, \hat{T}_1], \hat{T}_1] \; \Phi_0 \rangle \;. \tag{ex2'}$$

The first one of these examples obviously decomposes into the sum of two terms (following closely the second rule from above). The only interesting term remaining is the interdependence of nested commutators and product terms occurring in eq. (ex2'). According to the algorithm implemented this equation will be decomposed into two terms of the form:

$$\langle \Phi_0 | [[\hat{V}_N, \hat{T}_1], \hat{T}_1] \; \Phi_0 \rangle = \langle \Phi_0 | [[\hat{\sigma}^r_p \hat{\sigma}^s_q, \hat{\sigma}^a_i] \hat{\sigma}^b_j] \; \Phi_0 \rangle \tag{5.36}$$

$$= \langle \Phi_0 | [\hat{\sigma}^r_p [\hat{\sigma}^s_q \hat{\sigma}^a_i], \hat{\sigma}^b_j] \; \Phi_0 \rangle + \langle \Phi_0 | [[\hat{\sigma}^r_p \hat{\sigma}^a_i] \hat{\sigma}^s_q, \hat{\sigma}^b_j] \; \Phi_0 \rangle \;. \tag{5.37}$$

Of course, the two terms occurring in eq. 5.37 are expanded further because of the products occurring in the commutator expressions. This leads to the following equation:

$$\begin{aligned} \langle \Phi_0 | [[\hat{V}_N, \hat{T}_1], \hat{T}_1] \; \Phi_0 \rangle = {} & \langle \Phi_0 | \hat{\sigma}^r_p [[\hat{\sigma}^s_q, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \; \Phi_0 \rangle + \langle \Phi_0 | [\hat{\sigma}^r_p, \hat{\sigma}^b_j][\hat{\sigma}^s_q, \hat{\sigma}^a_i] \; \Phi_0 \rangle \\ & + \langle \Phi_0 | [\hat{\sigma}^r_p, \hat{\sigma}^a_i][\hat{\sigma}^s_q, \hat{\sigma}^b_j] \; \Phi_0 \rangle + \langle \Phi_0 | [[\hat{\sigma}^r_p, \hat{\sigma}^a_i], \hat{\sigma}^b_j] \hat{\sigma}^s_q \; \Phi_0 \rangle \;. \end{aligned} \tag{5.38}$$

The resulting terms can be dealt with on the basis of nested commutator expressions, leading to an increase of the number of terms by a factor of four for each expectation value. This results in an increase of the number of terms by a factor of sixteen, while the product expansion is responsible for two times a factor of two and the commutator evaluation contributes a factor of four. It is easily recognizable that the contribution of a product term to the total number of terms depends on the depth in terms of nested commutators the product occurs in.

In summary a product occurring inside a nested commutator expression has a recognizable effect on the number of terms. As stated in the example above the number of terms doubles for each level of commutator expressions if a product of two single substituters is involved.

Another example is discussed in the following, involving a threefold substitution:

$$\begin{aligned}\langle\Phi_0|[[\hat{F}_N,\hat{T}_3],\hat{T}_1]\ \Phi_0\rangle &= \langle\Phi_0|[[\hat{\sigma}_p^q,\hat{\sigma}_i^a\hat{\sigma}_j^b\hat{\sigma}_k^c],\hat{\sigma}_l^d]\ \Phi_0\rangle \qquad (5.39)\\ &= \langle\Phi_0|[\hat{\sigma}_i^a\hat{\sigma}_j^b[\hat{\sigma}_p^q,\hat{\sigma}_k^c],\hat{\sigma}_l^d]\ \Phi_0\rangle\\ &\quad+\langle\Phi_0|[\hat{\sigma}_i^a[\hat{\sigma}_p^q,\hat{\sigma}_j^b]\hat{\sigma}_k^c,\hat{\sigma}_l^d]\ \Phi_0\rangle\\ &\quad+\langle\Phi_0|[[\hat{\sigma}_p^q,\hat{\sigma}_i^a]\hat{\sigma}_j^b\hat{\sigma}_k^c,\hat{\sigma}_l^d]\ \Phi_0\rangle\ . \qquad (5.40)\end{aligned}$$

Evaluation of the above expression by means of an expansion of the products contained yields nine terms, namely:

$$\begin{aligned}\langle\Phi_0|[[\hat{F}_N,\hat{T}_3],\hat{T}_1]\ \Phi_0\rangle = &\langle\Phi_0|\hat{\sigma}_i^a\hat{\sigma}_j^b[[\hat{\sigma}_p^q,\hat{\sigma}_k^c],\hat{\sigma}_l^d]\ \Phi_0\rangle+\langle\Phi_0|\hat{\sigma}_i^a[\hat{\sigma}_j^b,\hat{\sigma}_l^d][\hat{\sigma}_p^q,\hat{\sigma}_k^c]\ \Phi_0\rangle\\ &+\langle\Phi_0|[\hat{\sigma}_i^a,\hat{\sigma}_l^d]\hat{\sigma}_j^b[\hat{\sigma}_p^q,\hat{\sigma}_k^c]\ \Phi_0\rangle+\langle\Phi_0|\hat{\sigma}_i^a[\hat{\sigma}_p^q,\hat{\sigma}_j^b][\hat{\sigma}_k^c,\hat{\sigma}_l^d]\ \Phi_0\rangle\\ &+\langle\Phi_0|\hat{\sigma}_i^a[[\hat{\sigma}_p^q,\hat{\sigma}_j^b],\hat{\sigma}_l^d]\hat{\sigma}_k^c\ \Phi_0\rangle+\langle\Phi_0|[[\hat{\sigma}_i^a,\hat{\sigma}_l^d][\hat{\sigma}_p^q,\hat{\sigma}_j^b]\hat{\sigma}_k^c]\ \Phi_0\rangle\\ &+\langle\Phi_0|[\hat{\sigma}_p^q,\hat{\sigma}_i^a]\hat{\sigma}_j^b[\hat{\sigma}_k^c,\hat{\sigma}_l^d]\ \Phi_0\rangle+\langle\Phi_0|[\hat{\sigma}_p^q,\hat{\sigma}_i^a][\hat{\sigma}_j^b,\hat{\sigma}_l^d]\hat{\sigma}_k^c\ \Phi_0\rangle\\ &+\langle\Phi_0|[[\hat{\sigma}_p^q,\hat{\sigma}_i^a],\hat{\sigma}_l^d]\hat{\sigma}_j^b\hat{\sigma}_k^c\ \Phi_0\rangle\ . \qquad (5.41)\end{aligned}$$

According to the previous discussion the number of terms scales as follows:

$$n = 2^{n_\text{nest}}\cdot\prod_{\text{op}\in\{\text{op}\}} n_\text{op}^d\ , \qquad (5.42)$$

where d is the depth the corresponding operator occurres in in terms of nested commutators and $\{\text{op}\}$ is the set of operators occuring in the expression.

5.6.2 Measurements

In the following section several measurements of computational demand of the presented term simplification in contrast to a straightforward implementation of WICK's theorem are presented and discussed.

5.6.2.1 Projection Levels

Despite the high computational demand of both methods it has been possible to study the effect of increasing projection levels employing the terms

$$\left\langle\Phi_0\left|\hat{D}_n^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_2]\ \ \Phi_0\right.\right\rangle,\qquad n\in\{2,3,4\}\ . \qquad (5.43)$$

Table 5.1: Total CPU time and maximum number of terms involved in the simplification of three different projections of the doubly nested commutator of the normal ordered two particle part of the hamiltonian with double excitations. Please note that the times and term numbers for the evaluation of WICK's theorem are scaled by the number of single substituters.

Term	CPU time / s		Maximum term number	
	Commutators	WICK	Commutators	WICK
$\hat{D}_2^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_2]$	70.04	9.70	5366	151552
$\hat{D}_3^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_2]$	630.25	380.21	41316	3833856
$\hat{D}_4^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_2]$	2739.91	8231.60	208080	63700992

Table 5.2: Timing analysis for a single module run. The results for WICK's theorem are obtained from table 5.1 with a scaling factor of $2^{-n_{\mathrm{op}}}$.

Term	CPU time / s		Ratio
	Commutators	WICK	
$\hat{D}_2^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_2]$	70.04	0.037891	1848.50
$\hat{D}_3^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_2]$	630.25	0.74260	848.71
$\hat{D}_4^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_2]$	2739.91	8.038	340.84

The results are presented in table 5.1. In order to compare the two methods for the case of spin free operators, the timing and term number results for the WICK contractions were obtained via $2^{n_{\mathrm{op}}}$ runs of the contraction module, where n_{op} is the number of single substitution operators involved.

It is noteworthy, that the presented term simplification overtakes the contraction via WICK's theorem during the transition from doubles to triples projections.

This fact could be assigned to the unfortunate additional scaling factor in the evaluation of the spin independent version of the WICK contraction. However, the unscaled results in table 5.2 reveal a constantly decreasing quotient between the times letting each module run only once[4]. In fact, an exponential extrapolation of the quotient suggests that the alternative algebraic approach overtakes a single run of the WICK contraction module in the vicinity of $n_{\mathrm{op}} = 20$. Unfortunately, operator strings that large can by far not be evaluated with both implementations.

[4] The time for a single run of the WICK module the timings obtained were divided by the number of runs. This leads to a decrease of noise due to overheads and other factors.

Table 5.3: Dependency of the maximal number of terms on altering the position of a two particle substitution. The timing for the WICK module was scaled by a factor of 2^8 in order to reduce noise and ensure comparability.

Term	CPU time / s		Maximum term number	
	Commutators	WICK	Commutators	WICK
$\hat{D}_2^\dagger[[\hat{V}_N,\hat{T}_2],\hat{T}_1],\hat{T}_1]$	18.7698	11.3918	1504	752
$\hat{D}_2^\dagger[[\hat{V}_N,\hat{T}_1],\hat{T}_2],\hat{T}_1]$	18.7256	11.2317	1504	752
$\hat{D}_2^\dagger[[\hat{V}_N,\hat{T}_1],\hat{T}_1],\hat{T}_2]$	18.7810	11.3284	1504	752

5.6.2.2 Position of Product Operators

The next analysis concentrates on the position of a $\hat{T}_2$ operator within a nested commutator. As discussed in the previous section, the position of the $\hat{T}_2$ operator should affect the performance of the commutator evaluation. Surprisingly, this is not the case in the actual timings in table 5.3. The number of maximal terms during the simplification stays constant while the computational time varies within a neglectable range.

A possible explanation for this phenomenon could be that in the first expansion step most of the terms generated by the expansion of the product term vanish due to upper left particle creator operators. In fact, closer inspection reveals that the number of terms after the first expansion step is almost constant.

Table 5.4: Comparison of the timing analyses for 100 module runs employing nested commutator expressions.

Term	CPU time / s		Ratio
	Commutators	WICK	
$\hat{D}_2^\dagger[[\hat{V}_N,\hat{T}_1]$	10.254	0.021	490.66
$\hat{D}_2^\dagger[[\hat{V}_N,\hat{T}_1],\hat{T}_1]$	36.004	0.250	144.19
$\hat{D}_2^\dagger[[[\hat{V}_N,\hat{T}_1],\hat{T}_1],\hat{T}_1]$	97.305	1.621	60.04
$\hat{D}_2^\dagger[[[[\hat{V}_N,\hat{T}_1],\hat{T}_1],\hat{T}_1],\hat{T}_1]$	118.674	4.562	26.01

5.6.2.3 Commutator Depth

The effect of the nesting depth of commutator expressions on the evaluation time has been investigated employing the following example terms:

$$\left\langle \Phi_0 \middle| \hat{D}_2^\dagger[\ldots[\hat{V}_N,\hat{T}_1]\ldots,\hat{T}_1] \;\; \Phi_0 \right\rangle \, . \tag{5.44}$$

The depth of the expressions ranged from singly nested to quadruply nested commutators. The results of the timing analysis are presented in tab. 5.4.

It can be seen that again Wick's theorem by far outperforms the presented method. However, as already pointed out before, the ratio of the evaluation times decreases for increasing operator numbers. Thus, it is possible that the performance of the commutator based term simplification could be better for than that of Wick's theorem for large operator numbers.

Chapter 6
Conclusion

This work investigated the development of an algebraic term simplification scheme for arbitrary excitation levels in single reference coupled cluster theory. It consisted of both the derivation and the implementation of a term simplification algorithm.

It turned out that the derivation of the coupled cluster working equations via Wick's theorem suffers from a very unfavourable scaling, at least in the case of spin independent operators. On the basis of this fact a more general form of manipulating second quantized operators was sought.

Employing the commutation relations that as well spin orbital as also spatial orbital substitution operators obey, a term simplification scheme was developed that distinguishes between the two operator types only at the very last contraction step. All other steps in the presented method are of a general form, i.e. independent of the nature of the operators involved.

An algorithm for the term simplification could be derived that has an iterative character and relies on the evaluation and subsequent generation of commutator expressions. The evaluation steps reduce the size of an operator string by one at least and generate contractions (i.e. collapsing summations) between indices contained in different substitution operators. Application of this scheme to an operator expression until a stable result is reached yields the fully contracted terms known from the evaluation of Wick's theorem.

The algorithm presented could be implemented into the Quantum Objects Library program package developed in the Cologne Quantum Chemistry Group. It makes excessive use of dynamic programming concepts. This has the advantage that arbitrarily nested expressions can be dealt with as the type evaluation occurs at runtime of the program. However, the price to pay for this generality of the program is a large overhead due to the fact that all type specifications and identifications have to occur at runtime.

Timing analyses have shown that for the test cases concidered the implemented algorithm could hardly compete with a straightforward implementation of Wick's theorem. Nevertheless, the analyses also suggest that for larger operator strings the presented algorithm could possibly outperform the Wick contraction algorithm. Especially in the case of spin independent operators one can be fairly optimistic. As the commutator based term simplification does not change its scaling behaviour in this case, the relative efficiency with respect to Wick's theorem rises dramatically with the size of the operator string to be evaluated.

It should be noted that the term simplification presented is not complete, as there are still many redundant terms (by means of index symmetries) are generated. To overcome this issue, one would have to implement an identification algorithm for the redundancies.

Maybe the most efficient way to identify the redundant terms is to translate the terms to their diagrammatic representation, canonicalize the diagrams and translate back. This type of algorithm is already implemented in the QOL for the spin orbital case. However, a generalization to the symmetry properties of the spin independent tensor quantities is a highly non-trivial task.

Bibliography

[1] Coester, F. (1958) *Nucl. Phys.* **7**, 421. (Cited on pages 11 and 27.)

[2] Coester, F. and Kümmel, H. (1960) *Nucl. Phys.* **17(0)**, 477. (Cited on pages 11 and 27.)

[3] Čížek, J. (1966) *J. Chem. Phys.* **45(11)**, 4256. (Cited on pages 11 and 38.)

[4] Čížek, J. and Paldus, J. (1971) *Int. J. Quantum Chem.* **5**, 359. (Cited on pages 11 and 38.)

[5] Čížek, J. and Paldus, J. (1980) *Phys. Scr.* **21(3-4)**, 251. (Cited on pages 11 and 38.)

[6] Bartlett, R. (1981) *Ann. Rev. Phys. Chem.* **32**, 359. (Cited on page 11.)

[7] Bartlett, R. J. (1989) *J. Phys. Chem.* **93(5)**, 1697. (Cited on page 11.)

[8] Bartlett, R. J. and Musiał, M. (2007) *Rev. Mod. Phys.* **79**, 291. (Cited on page 11.)

[9] Purvis, G. and Bartlett, R. (1982) *J. Chem. Phys.* **76**, 1910. (Cited on pages 11 and 38.)

[10] Werner, H.-J., Knowles, P. J., Lindh, R., Manby, F. R., Schütz, M., Celani, P., Korona, T., Rauhut, G., Amos, R. D., Bernhardsson, A., Berning, A., Cooper, D. L., Deegan, M. J. O., Dobbyn, A. J., Eckert, F., Hampel, C., Hetzer, G., Lloyd, A. W., McNicholas, S. J., Meyer, W., Mura, M. E., Nicklass, A., Palmieri, P., Pitzer, R., Schumann, U., Stoll, H., Stone, A. J., Tarroni, R., and Thorsteinsson, T. , MOLPRO, version 2002.6, a package of *ab initio* programs, see `http://www.molpro.net`. (Cited on pages 12 and 39.)

[11] Karlström, G., Lindh, R., Malmqvist, P.-Å., Roos, B. O., Ryde, U., Veryazov, V., Widmark, P.-O., Cossi, M., Schimmelpfennig, B., Neogrady, P., and Seijo., L. (2003) *Computational Material Science* **28**, 222 , *Molcas: A Program Package for Computational Chemistry.* (Cited on pages 12 and 39.)

[12] Turbomole TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from
`http://www.turbomole.com`. (Cited on pages 12 and 39.)

[13] Scheiner, A. C., Scuseria, G. E., Rice, J. E., Lee, T. J., and Schaefer III, H. F. (1987) *J. Chem. Phys.* **87**, 5361. (Cited on pages 12 and 39.)

[14] Monkhorst, H. (1977) *Int. J. Quantum Chem. Symp.* **11**, 421. (Cited on page 12.)

[15] Perera, S., Nooijen, M., and Bartlett, R. (1996) *J. Chem. Phys.* **104**, 3290. (Cited on page 12.)

[16] Gauss, J. and Stanton, J. (1995) *J. Chem. Phys.* **102**, 251. (Cited on page 12.)

[17] Gauss, J. (193) *J. Chem. Phys.* **99**, 3629. (Cited on page 12.)

[18] Noga, J. and Bartlett, R. (1987) *J. Chem. Phys.* **86**, 7041. (Cited on page 12.)

[19] Noga, J. and Bartlett, R. (1988) *J. Chem. Phys.* **89**, 3401. (Cited on page 12.)

[20] Trucks, G., Noga, J., and Bartlett, R. J. (1988) *Chem. Phys. Lett.* **145**, 548. (Cited on page 12.)

[21] Kucharski, S. and Bartlett, R. (1992) *J. Chem. Phys.* **97**, 4282. (Cited on page 12.)

[22] Musiał, M., Kucharski, S., and Bartlett, R. (2000) *Chem. Phys. Lett.* **320**, 542. (Cited on page 12.)

[23] Musiał, M., Kucharski, S., and Bartlett, R. (2002) *J. Chem. Phys.* **116**, 4382. (Cited on page 12.)

[24] Hanrath, M. and Engels-Putzka, A. (2010) *J. Chem. Phys.* **133**, 064108. (Cited on page 12.)

[25] Engels-Putzka, A. and Hanrath, M. (2011) *J. Chem. Phys.* **134**, 124106. (Cited on page 12.)

[26] Kallay, M. and Surjan, P. R. (2001) *J. Chem. Phys.* **115**, 2945. (Cited on page 12.)

[27] Hirata, S. and Bartlett, R. (2000) *Chem. Phys. Lett.* **321**, 216. (Cited on page 12.)

[28] Olsen, J. (Cited on page 12.)

[29] Lyakh, D., Ivanov, V., and Adamowicz, L. (2005) *J. Chem. Phys.* **122**, 024108. (Cited on page 12.)

[30] Mukherjee, D., Moitra, R. K., and Mukhopadhyay, A. (1977) *Mol. Phys.* **33**, 955. (Cited on page 12.)

[31] Mukherjee, D., Moitra, R. K., and Mukhopadhyay, A. (1975) *Mol. Phys.* **30(6)**, 1861. (Cited on page 12.)

[32] Lindgren, I. (1978) *Int. J. Quantum Chem. Symp.* **12**, 33. (Cited on page 12.)

[33] Lindgren, I. and Mukherjee, D. (1987) *Phys. Reports* **151**, 93. (Cited on page 12.)

[34] Mukherjee, D. and Pal, S. (1989) *Adv. Quantum Chem.* **20**, 291. (Cited on page 12.)

[35] Jeziorski, B. and Monkhorst, H. J. (1981) *Phys. Rev. A: At. Mol. Opt. Phys.* **24**, 1668. (Cited on page 12.)

[36] Jeziorski, B. and Paldus, J. (1988) *J. Chem. Phys.* **88**, 5673. (Cited on page 12.)

[37] Paldus, J., Piecuch, P., Pylypow, L., and Jeziorski, B. (1993) *Phys. Rev. A* **47**, 2738. (Cited on page 12.)

[38] Kucharski, S. and Bartlett, R. (1991) *J. Chem. Phys.* **95**, 8227. (Cited on page 12.)

[39] Balkova, A., Kucharski, S., Meisner, L., and Bartlett, R. (1991) *Theor. Chem. Acc.* **80**, 335. (Cited on page 12.)

[40] Balkova, A., Kucharski, S., Meisner, L., and Bartlett, R. (1991) *J. Chem. Phys.* **95**, 4311. (Cited on page 12.)

[41] Hanrath, M. (2005) *J. Chem. Phys.* **123(8)**, 084102. (Cited on page 12.)

[42] Li, X. and Paldus, J. (1997) *J. Chem. Phys.* **107(16)**, 6257. (Cited on page 12.)

[43] Oliphant, N. and Adamowicz, L. (1991) *J. Chem. Phys.* **94(2)**, 1229. (Cited on page 12.)

[44] Maitra, R., Sinha, D., and Mukherjee, D. (2012) *J. Chem. Phys.* **137**, 024105. (Cited on page 12.)

[45] Hariharan, P. and Pople, J. (1973) *Theoret. Chim. Acta* **28**, 213. (Cited on page 13.)

[46] Matthews, D., Gauss, J., and Stanton, J. (2013) *J. Chem. Theory Comp.* **6**, 2567. (Cited on pages 14 and 39.)

[47] Matthews, D. and Stanton, J. (2013) to be published. (Cited on pages 14 and 39.)

[48] Jordan, P. and Klein, O. (1927) *Z. Phys.* **45**, 751. (Cited on pages 17 and 28.)

[49] Helgaker, T., Jørgensen, P., and Olsen, J. (2004) Molecular Electronic-Structure Theory, John Wiley & Sons Ltd, Chichester. (Cited on page 17.)

[50] Kutzelnigg, W. (2002) Einführung in die Theoretische Chemie, Wiley-VCH, Weinheim. (Cited on page 17.)

[51] Szabo, A. and Ostlund, N. S. (1989) Modern Quantum Chemistry (First Edition), Dover Publications, Inc., New York. (Cited on page 17.)

[52] B. O. Roos and P. O. Widmark, (ed.) (2003) European Summer School in Quantum Chemistry 2003 Book I, University of Lund, Lund. (Cited on page 17.)

[53] B. O. Roos and P. O. Widmark, (ed.) (2003) European Summer School in Quantum Chemistry 2003 Book II, University of Lund, Lund. (Cited on page 17.)

[54] Bartlett, R. J. and Shavitt, I. (2009) Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory, Cambridge University Press, Cambridge, United Kingdom. (Cited on pages 17, 29, 30 and 36.)

[55] Schrödinger, E. (1926) *Ann. Phys.* **79**, 361. (Cited on page 18.)

[56] Schrödinger, E. (1926) *Ann. Phys.* **79**, 489. (Cited on page 18.)

[57] Schrödinger, E. (1926) *Ann. Phys.* **79**, 734. (Cited on page 18.)

[58] Schrödinger, E. (1926) *Ann. Phys.* **81**, 109. (Cited on page 18.)

[59] Born, M. and Oppenheimer, R. (1927) *Ann. Phys.* **20**, 457. (Cited on page 18.)

[60] Wang, Q.-D. (1991) *Celest. Mech. Dyn. Astron.* **50**, 73. (Cited on page 19.)

[61] Bosch, S. (2001) Lineare Algebra, Springer-Verlag, Berlin, Heidelberg, New York. (Cited on page 20.)

[62] Slater, J. C. (1929) *Phys. Rev.* **34**, 1293. (Cited on page 20.)

[63] Hartree, D. R. (1928) *Math. Proc. Cambridge Philos. Soc.* **24**, 89. (Cited on page 21.)

[64] Fock, V. (1930) *Z. Phys.* **61**, 126. (Cited on page 21.)

[65] Roothaan, C. (1951) *Rev. Mod. Phys.* **22**, 69. (Cited on page 22.)

[66] Hall, G. (1951) *Proc. Roy. Soc. London A* **28**, 541. (Cited on page 22.)

[67] Booth, G. H., Thom, A. J. W., and Alavi, A. (2009) *J. Chem. Phys.* **131**, 054106. (Cited on page 24.)

[68] Davidson, E. R. (1975) *J. of Comp. Phys.* **17(1)**, 87. (Cited on page 24.)

[69] Dirac, P. A. M. (1927) *Proc. R. Soc. (London) A* **114**, 243. (Cited on page 28.)

[70] Jordan, P. and Wigner, E. (1928) *Z. Phys.* **47**, 631. (Cited on page 28.)

[71] Wick, G. (1950) *Phys. Rev.* **80**, 268. (Cited on page 30.)

[72] Baker (1905) *Proc. London Math. Soc. Ser. 2* **3**, 24. (Cited on page 33.)

[73] Campbell (1897) *Proc. London Math, Soc.* **28**, 381. (Cited on page 33.)

[74] Hausdorff (1906) *Ber. Verhandl. Sächs. Akad. Wiss. Leipzig Math.-Naturw. Kl.* **58**, 19. (Cited on page 33.)

[75] Feynman, R. P. (1949) *Phys. Rev.* **76**, 749. (Cited on page 34.)

[76] Feynman, R. P. (1949) *Phys. Rev.* **76**, 769. (Cited on page 34.)

[77] Hugenholz (1957) *Physica* **23**, 481. (Cited on page 34.)

[78] Goldstone, J. (1957) *Proc. R. Soc. London A* **239**, 267. (Cited on page 34.)

[79] Brandow, B. H. (1967) *Rev. Mod. Phys.* **39**, 771. (Cited on page 34.)

[80] Paldus, J. (1977) *J. Chem. Phys.* **67(1)**, 303. (Cited on page 38.)

[81] Adams, B. and Paldus, J. (1979) *Phys. Rev. A* **20**, 1. (Cited on page 38.)

[82] Paldus, J., Čížek, J., and Takahashi, M. (1984) *Phys. Rev. A* **30**, 2193. (Cited on page 38.)

[83] Piecuch, P. and Paldus, J. (1992) *Theor. Chem. Acc.* **83**, 69. (Cited on page 38.)

[84] Scuseria, G. E., Scheiner, A. C., Lee, T. J., Rice, J. E., and Schaefer III, H. F. (1987) *J. Chem. Phys.* **86(5)**, 2881. (Cited on page 39.)

[85] Scuseria, G. E., Janssen, C. L., and Schaefer III, H. F. (1988) *J. Chem. Phys.* **89(12)**, 7382. (Cited on page 39.)

[86] Scuseria, G. E. and Schaefer III, H. F. (1988) *Chem. Phys. Lett.* **152**, 382. (Cited on page 39.)

[87] Stanton, J., Gauss, J., Harding, M., Szalay, P., Auer, A., Bartlett, R., Benedikt, U., Berger, C., Bernholdt, D., Bomble, Y., Cheng, L., Christiansen, O., Heckert, M., Heun, O., Huber, C., Jagau, T.-C., Jonsson, D., Jusélius, J., Klein, K., Lauerdale, W., Matthews, D., Metzroth, T., Mück, L., O'Neill, D., Price, D., Prochnow, E., Puzzarini, C., Ruud, K., Schiffmann, F., Schwalbach, W., Stopkowicz, S., Tajti, A., Vázquez, J., Wang, F., and Watts, J. , CFOUR, *Coupled-Cluster techniques for Computational Chemistry*, a quantum-chemical program with the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Jensen, P. Jørgensen and J. Olsen), and ECP routines by Mitin, A.V., van Wüllen, C.. For the current version, see `http://www.cfour.de`. (Cited on page 39.)

[88] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, Jr., J. A., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B.,

Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., and Pople, J. A. Gaussian 03, Revision D.02 Gaussian, Inc., Wallingford CT, 2004. (Cited on page 39.)

[89] Hampel, C., Peterson, K. A., and Werner, H.-J. (1992) *Chem. Phys. Lett.* **190**, 1. (Cited on page 39.)

[90] Paldus, J. (1974) *J. Chem. Phys.* **61**, 5321. (Cited on page 43.)

[91] Paldus, J. and Jeziorski, B. (1988) *Theor. Chem. Acc.* **73**, 81. (Cited on page 43.)

[92] Matsen, F. A. and Pauncz, R. (1986) The Unitary Group in Quantum Chemistry, Elsevier, Amsterdam. (Cited on page 43.)

[93] Cassam-Chenai, P. (2002) The real generators of the unitary group, volume **14**, of Topics in Molecular Organization and Engineering, pp. 77–78, Springer Netherlands. (Cited on page 43.)

[94] Bartlett, R. and Noga, J. (1988) *Chem. Phys. Lett.* **150**, 29. (Cited on page 43.)

[95] Bartlett, R., Kucharski, S., and Noga, J. (1989) *Chem. Phys. Lett.* **155**, 133. (Cited on page 43.)

[96] Hanrath, M. Equivalence class decomposition of contraction patterns in Wicks theorem: Exploiting tensor antisymmetry, unpublished (2013). (Cited on page 78.)

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Ich verbleibe im Gedenken an Benno Borchardt, Agnes und Josef Pape.

Köln, im September 2013

Appendix B
Erklärung

Ich versichere, dass ich die von mir vorgelegte Dissertation selbständig angefertigt, die benutzten Quellen und Hilfsmittel vollständig angegeben und die Stellen der Arbeit — einschließlich Tabellen, Karten und Abbildungen —, die anderen Werken im Wortlaut oder dem Sinn nach entnommen sind, in jedem Einzelfall als Entlehnung kenntlich gemacht habe; dass diese Dissertation noch keiner anderen Fakultät oder Universität zur Prüfung vorgelegen hat; dass sie — abgesehen von unten angegebenen Teilpublikationen — noch nicht veröffentlicht worden ist sowie, dass ich eine solche Veröffentlichung vor Abschluss des Promotionsverfahrens nicht vornehmen werde. Die Bestimmungen der Promotionsordnung sind mir bekannt. Die von mir vorgelegte Dissertation ist von Herrn Prof. Dr. Michael Dolg betreut worden. Ich versichere, dass ich alle Angaben wahrheitsgemäß nach bestem Wissen und Gewissen gemacht habe und ich verpflichte mich, jedmögliche, die obigen Angaben betreffende, Veränderung dem Dekanat unverzüglich mitzuteilen.

(Daniel Pape)

Appendix C
Lebenslauf

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