A Variant of Multi-Reference Coupled Cluster for Density Matrix Renormalisation Group
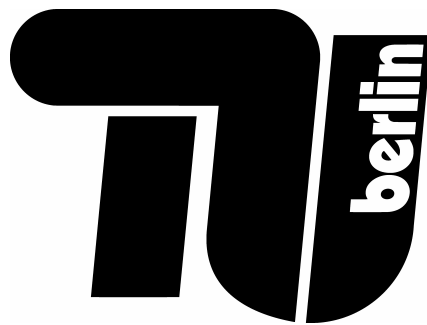
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A thesis submitted for the degree of

Master of Science

in Mathematics

Statement of Authorship

This thesis has been submitted for the degree of Master of Science in Mathematics. I, the undersigned, hereby declare that:

- I am the sole author of this thesis.

- I have fully acknowledged and referenced the ideas and work of others, whether published or unpublished, in my thesis.

- I have prepared my thesis specifically for the degree of Master of Science while under supervision at the Technical University of Berlin.

- My thesis does not contain work extracted from a thesis, dissertation or research paper previously presented for another degree or diploma at this or any other university.

Berlin, July 17, 2017: _____
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Abstract

We present a first analysis of the DMRG-TCC, a multi-reference method for accurate treatment of strongly correlated electron systems, which combines the coupled cluster theory with the density matrix renormalisation group method [1]. We present a formulation of the tailored coupled cluster method in a mathematical framework. For the analysis of the tailored coupled cluster method we follow the structure presented in [2], where due to the static electron correlation the HOMO-LUMO gap needs to be replaced by a more general CAS-EXT gap. Subsequently, we show that under certain assumptions a local version of Zarantonello's theorem is applicable to the tailored coupled cluster function. This guarantees locally unique solutions and quasi optimal error estimates. In addition, we give a rigorous analytical treatment of the truncated tailored coupled cluster method, the TCCSD. Unlike in the case of CCSD, our analysis shows that linked and unlinked tailored coupled cluster equations are in general not equivalent. The equivalence holds in case of using Brueckner orbitals [3, 4, 5] or an orbital-adaptive coupled cluster method [6]. Using one of these approaches yields a smaller set of amplitude equations in the unlinked formulation.

Zusammenfassung

Wir präsentieren eine erste Analyse der DMRG-TCC-Methode, einer Multi-Referenzmethode mit hoher Genauigkeit für stark korrelierte Elektronensysteme, welche die Coupled-Cluster-Methode mit der Density-Matrix-Renormalisation-Group-Methode (DMRG) verbindet [1]. Zunächst geben wir eine mathematische Formulierung der Tailored-Coupled-Cluster-Methode an. Für die Analyse der Tailored-Coupled-Cluster-Methode folgen wir den Schritten aus [2], wobei wir aufgrund der starken Korreliertheit des Elektronensystems die HOMO-LUMO-Lücke durch eine allgemeinere CAS-EXT-Lücke ersetzen müssen. Anschließend zeigen wir, dass unter bestimmten Annahmen eine lokale Version des Satzes von Zarantonello auf die Tailored-Coupled-Cluster-Funktion angewendet werden kann. Dies garantiert lokal eindeutige Lösungen und quasioptimale Fehlerabschätzungen. Des Weiteren präsentieren wir eine rigorose analytische Behandlung der abgeschnittenen Tailored-Coupled-Cluster-Methode (TCCSD). Anders als bei der CCSD-Methode zeigt unsere Analyse, dass die Linked- und Unlinked-Tailored-Coupled-Cluster-Gleichungen nicht äquivalent sind. Die Äquivalenz dieser Gleichungen gilt jedoch bei Verwendung von Brueckner-Orbitalen [3, 4, 5] oder der orbitaladaptiven Coupled-Cluster-Methode [6]. Unter Verwendung einer dieser Ansätze lassen sich die Unlinked-Amplitudengleichungen weiter vereinfachen.

Contents

1 Introduction

In 1927 a collection of information was published by Niels Bohr and Werner Heisenberg that postulated how the mathematical formalism of quantum mechanics is supposed to be understood in terms of everyday language [7]. This publication gave a unique interpretation of wave functions, Hamilton operators and many other quantities. This so-called *Copenhagen interpretation* was the start of a period full of new theories and models which aimed to describe physical systems. Since then there has been huge progress in the field of theoretical physics, especially in quantum theory of many particle physics. In 1929, Paul Dirac stated that 'the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are [...] completely known' [8]. Nevertheless, the development of 'approximate practical methods of applying quantum mechanics', demanded by him in the same breath, is still a highly active field of research in the overlap of physics, chemistry, applied mathematics and computer science. With the increasing availability of ever more powerful computers, numerical simulations have become increasingly common, and are now a standardized tool to understand and predict the behaviour of large or otherwise complicated systems. Due to this development, calculations of theoretical chemistry and molecular physics have become competitive with practical experiments, or at the very least allow useful predictions of empirical parameters assisting practical investigations. The main equation used in quantum chemical and molecular physics calculations is the molecular Schrödinger equation. This equation is high-dimensional, thus computationally demanding, and requires extremely high accuracy in order to obtain results that can be utilised in practice. As a result, small to medium sized quantum chemical problems still push the limits of commonly available computational resources.

The *coupled cluster* method was derived by the nuclear physicists Coester and Kümmel in the 1950's [9, 10, 11, 12]. Due to the publications by Sinanoğlu, Čížek, Paldus and Shavitt [13, 14, 15] the idea of the *coupled cluster* method was transferred from nuclear physics to the field of electronic structure in the 1960's. It is today one of the most applied tools in the calculation of ground state solutions of the stationary N-electron Schrödinger equation, when needing results of high-accuracy. In the case of the CCSD(T) method [16], which can be applied to small and medium sized molecules with reasonable computational effort, the *coupled cluster* method often provides results which are within the error bars of

corresponding practical experiments [17]. The *coupled cluster* method is therefore often referred to as the *golden standard of quantum chemistry.*

However, a disadvantage of this method is that it calculates a single-reference approximation to the solution. As a result, this method is unfit for strongly correlated electronic systems. There have been several attempts to correct this flaw [18]. One attempt is the so called *externally corrected coupled cluster* method. The idea is to combine the *single-reference coupled cluster* method with a *full configuration interaction* solution of a subsystem covering all the static correlation [19]. This keeps the computational costs low as the *full configuration interaction* solution is calculated only for a subsystem and guarantees the high accuracy of the *coupled cluster* method for the dynamical correlation of the system. This multi-reference approach gained recent attention when the *full configuration interaction* solution was approximated by the *density matrix renormalisation group* [1].

In this thesis we will present a first analysis of the *tailored coupled cluster* method. First, we will give a short introduction to the mathematical framework of the electronic Schrödinger equation and to the Cauchy–Dunford calculus. Secondly we will present the quantum chemical calculation schemes which are used to define the *tailored coupled cluster* method. We will start by presenting the *Hartree–Fock* method, which will be the starting point for the *coupled cluster* method. Thereafter, we will introduce the *full configuration interaction* method. Having described these two standard quantum chemical approaches we will move on to the *coupled cluster* method. The steps we will use in the analysis of the *coupled cluster* method will be of utmost importance for the later analysis of the *tailored coupled cluster* method. This is why we will present them in a very detailed manner. Finally, we will define the *tailored coupled cluster* method in a mathematical framework and will present a first analysis.

2 Mathematical Framework

2.1 Cauchy–Dunford Calculus

In this section we give a short introduction to the *Cauchy–Dunford calculus*. This functional calculus for operators acting on finite dimensional Banach spaces, plays an important role in the formulation of the *coupled cluster* method, more precisely, in the definition of the *cluster operator*. The *Cauchy–Dunford calculus* is one way of defining complex valued analytic functions on the space of linear and bounded operators by using a Cauchy's integral formula like approach. The sequel is a brief summery of a paragraph in [20]. We emphasise that the focus of this thesis lies on the analysis of the *coupled cluster* and the *tailored coupled cluster* method defined on finite dimensional ansatz spaces. We therefore omit the proofs in this section and only give a short summery of the objects and structures that the *Cauchy–Dunford calculus* over finite dimensional Banach spaces makes use of.
We start by the definition of the spectrum of a bounded linear operator.

Definition 2.1. *Let T be a bounded linear operator acting on a finite dimensional complex Banach space X and I be the identity operator on X. The **spectrum of** T, denoted by $\sigma(T)$, is the set of all $\lambda \in \mathbb{C}$ for which the operator $\lambda I - T$ is not boundedly invertible. The **index** $\nu(z)$ of a complex number z is the smallest non-negative integer ν such that $(zI - T)^{\nu} x = 0$ for every x for which $(zI - T)^{\nu+1} x = 0$.*

With this definition we are able to characterise those complex functions that are analytic in an open set containing the spectrum $\sigma(T)$ of some bounded, linear and Banach-space-valued operator T. These functions are of utmost importance as they classify the set of function for which the *Cauchy-Dunford-calculus* holds.

Definition 2.2. *We denote by $\mathscr{F}(T)$ the class of all complex functions which are analytic in some open set containing $\sigma(T)$.*

Remark 2.3. *In the above definition the open set containing the spectrum does not have to be connected.*

As the functions $\mathscr{F}(T)$ are analytic functions, we can find a local power series expansion. In particular, for any $f \in \mathscr{F}(T)$ we find a polynomial p such that $f^{(m)}(z) = p^{(m)}(z)$, $m \leq \nu(z) - 1$, for each $z \in \sigma(T)$. We then define $f(T) = p(T)$.

The following theorem shows that this definition is well-defined.

Theorem 2.4. *If p and q are polynomials, then $p(T) = q(t)$ if and only if $p - q$ has a zero of order $\nu(z)$ at each point $z \in \sigma(T)$.*

Before stating the main theorem of the *Cauchy–Dunford calculus*, we present two properties that the class of functions $\mathscr{F}(T)$ has. The first theorem shows algebraic structures of $\mathscr{F}(T)$, as well as properties of operators mapped by functions in $\mathscr{F}(T)$.

Theorem 2.5. *Be $f, g \in \mathscr{F}(T)$ and $z_1, z_2 \in \mathbb{C}$. Then holds*

i) $z_1 f + z_2 g \in \mathscr{F}(T)$ *and* $(z_1 f + z_2 g)(T) = z_1 f(T) + z_2 g(T)$

ii) $f \cdot g \in \mathscr{F}(T)$ *and* $(f \cdot g)(T) = f(T) \cdot g(T)$

iii) if $f(z) = \sum_{n=0}^{m} a_n z^n$ *then* $f(T) = \sum_{n=0}^{m} a_n T^n$

iv) $f(t) = 0$ *if and only if* $f^{(m)}(z) = 0$ *for every* $z \in \sigma(T)$ *and every* $0 \leq m \leq \nu(z) - 1$.

The second theorem shows how operators mapped by functions in $\mathscr{F}(T)$ can be expanded by a finite series around the spectral points of the operator T. This property is a key element for the proof of the *Cauchy–Dunford* theorem.

Theorem 2.6. *Be $f \in \mathscr{F}(T)$. Then*

$$f(T) = \sum_{z \in \sigma(T)} \sum_{n=0}^{\nu(z)-1} \frac{(T - zI)^n}{n!} f^{(n)}(z) E(z) \ , \tag{2.1}$$

where $E(z) = e_z(T)$ with $e_z(T)$ is identically equal to one in a neighbourhood of z and identically zero in a neighbourhood of each point of $\sigma(T) \cap \{z\}^c$.

Finally, at the end of this short introductory section to a part of the operator theory background for the *coupled cluster* formalism, we state the main theorem of the *Cauchy–Dunford calculus*.

Theorem 2.7 (Cauchy–Dunford). *Let $f \in \mathscr{F}(T)$ be analytic in a domain containing the closure of an open set U containing $\sigma(T)$, and suppose that the boundary B of U consists of a finite number of closed rectifiable Jordan curves, oriented in the positive sense. Then $f(T)$ may be expressed as a Riemann contour integral over B by the following formula*

$$f(T) = \frac{1}{2\pi i} \int_B f(z)(zI - T)^{-1} dz \ . \tag{2.2}$$

Remark 2.8. *The Cauchy–Dunford calculus holds in particular true for U whose boundary is a circle.*

2.2 Hamilton Operator

The Hamilton operator is the central object of quantum mechanics. Therefore, we give a brief introduction to this differential operator and its domain. For the sake of simplicity we shall only describe time independent and real valued problems. The following construction is geared to [21]. For more detailed information on this differential operator see [22, 23, 24].

We start this section by defining the Sobolev space H^1, which results in being the appropriate space for the definition of the Hamilton operator. To define this function space we use the *multi-index notation*.

Definition 2.9. *An n-dimensional multi-index is an n-tuple*

$$\alpha = (\alpha_1, \alpha_2, \ldots, \alpha_n) \tag{2.3}$$

of non-negative integers (i.e. an element of the n-dimensional set of natural numbers, denoted by $\mathbb{N}_0^n$). For a multi-index $\alpha \in \mathbb{N}_0^n$, $x = (x_1, x_2, \ldots, x_n) \in \mathbb{R}^n$ and an $|\alpha|$-times continuously differentiable function $f : \mathbb{R}^n \to \mathbb{C}$ we define:

(i) *the sum of components (absolute value) of a multi-index by*

$$|\alpha| = \alpha_1 + \alpha_2 + \cdots + \alpha_n \tag{2.4}$$

(ii) *the multi-index power of a vector by*

$$x^\alpha = x_1^{\alpha_1} x_2^{\alpha_2} \ldots x_n^{\alpha_n} \tag{2.5}$$

(iii) *the multi-index derivative by*

$$D^\alpha f = D_1^{\alpha_1} D_2^{\alpha_2} \ldots D_n^{\alpha_n} f \, , \tag{2.6}$$

where $D_i^{\alpha_i} f$ denotes the partial derivative of f with respect to the i-th component of f to the order α_i.

Using this notation we can define the *space of rapidly decreasing functions on $\mathbb{R}^n$*. This space, also known as *Schwartz space*, plays a central role in Fourier analysis and provides an approach to *Sobolev spaces*.

Definition 2.10. *The **Schwartz space** or **space of rapidly decreasing functions on** $\mathbb{R}^n$ is the function space*

$$\mathcal{S}\left(\mathbb{R}^n\right) = \{f \in \mathcal{C}^\infty(\mathbb{R}^n) : \|f\|_{\alpha,\beta} < \infty \quad \forall \alpha, \beta\}, \tag{2.7}$$

where α, β are multi-indices, $\mathcal{C}^\infty(\mathbb{R}^n)$ is the set of smooth functions from $\mathbb{R}^n$ to $\mathbb{C}$, and

$$\|f\|_{\alpha,\beta} = \sup_{x \in \mathbb{R}^n} \left|x^\alpha D^\beta f(x)\right|. \tag{2.8}$$

The *Sobolev space $H^1(\mathbb{R}^n)$*, and therewith the domain of the Hamilton operator, is a closure of the Schwartz space under a specific norm. The norm which yields the Sobolev space is the $H^1(\mathbb{R}^n)$-*norm*.

Definition 2.11. *The map*

$$
\begin{aligned}
&\| \cdot \|^2_{H^1(\mathbb{R}^n)} : L^2(\mathbb{R}^n) \cap \mathcal{C}^1(\mathbb{R}^n) \to \mathbb{R}; \\
&u \mapsto \|u\|^2_{H^1(\mathbb{R}^n)} = \|u\|^2_{L^2(\mathbb{R}^n)} + \|\nabla u\|^2_{(L^2(\mathbb{R}^n))^n} ,
\end{aligned} \tag{2.9}
$$

*is called $H^1(\mathbb{R}^n)$-**norm**. Here $\| \cdot \|_{L^2(\mathbb{R}^n)}$ is the norm induced by the $L^2(\mathbb{R}^n)$ scalar product $\langle \cdot, \cdot \rangle_{L^2(\mathbb{R}^n)}$ and $\mathcal{C}^1(\mathbb{R}^n)$ denotes the space of continuously differentiable functions. The second part in the above definition is also called the $H^1(\mathbb{R}^n)$ **seminorm** and is denoted by $|u|_{H^1(\mathbb{R}^n)} := \|\nabla u\|_{(L^2(\mathbb{R}^n))^n}$.*

Using the above defined $H^1(\mathbb{R}^n)$-norm and the Schwartz space we define the *Sobolev space $H^1(\mathbb{R}^n)$* as follows:

Definition 2.12. *The closure of the Schwartz space under the $H^1(\mathbb{R}^n)$-norm is called **Sobolev space** or $H^1(\mathbb{R}^n)$*

$$H^1(\mathbb{R}^n) = \overline{\mathcal{S}(\mathbb{R}^n)}^{\ \|\cdot\|_{H^1(\mathbb{R}^n)}} . \tag{2.10}$$

Having defined the Sobolev space $H^1(\mathbb{R}^n)$ we state the following useful functional analytic result:

Theorem 2.13. *Let $\mathcal{D}(\mathbb{R}^n) = \mathcal{C}_0^\infty(\mathbb{R}^n)$ be the space of all infinitely often differentiable functions with compact support on $\mathbb{R}^n$. Then $\mathcal{D}(\mathbb{R}^n)$ is dense in $H^1(\mathbb{R}^n)$*

A proof for this theorem and further introduction to the theory of Sobolev spaces is given in [25].
As mentioned, the Hamilton operator is a differential operator. When referring to the Hamilton operator, we always refer to a specific Hamilton operator, namely the one considered in this thesis. In general, a Hamilton operator is defined as follows.

Definition 2.14. *A **Hamilton operator** is an elliptic differential operator, formally defined by*

$$(Hu)(x) = -\frac{1}{2}\Delta u(x) + V(x)u(x) \ . \tag{2.11}$$

*The function $V : \mathbb{R}^n \to \mathbb{R}$ is called the **potential** of the operator.*

A broader and more detailed description of such differential operators can be found in [26, 27, 28, 29, 30].

In this thesis we consider the *electronic Schrödinger equation*. To define the respective Hamilton operator, we take a closer look at the Hamilton operator of a molecule without any external electromagnetic field. We consider a molecule consisting of M nucleus with mass M_n and charge Z_n, where $n \in \{1, ..., M\}$ and N electrons of mass m. The Hamilton operator of this system is given by:

$$
\begin{aligned}
H_{full} = &\sum_{l=1}^{N} \frac{-\hbar^2 \Delta_{x,l}}{2m} + \sum_{n=1}^{M} \frac{-\hbar^2 \Delta_{R,n}}{2M_n} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i,j=1;i\neq j}^{N} \frac{e^2}{|x_i - x_j|} \\
&+ \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n,n'=1;n\neq n'}^{M} \frac{Z_n Z_{n'} e^2}{|R_n - R_{n'}|} - \frac{1}{4\pi\epsilon_0} \sum_{n=1}^{M} \sum_{i=1}^{N} \frac{Z_n e^2}{|x_i - R_n|} \ .
\end{aligned}
\tag{2.12}
$$

The Hamilton operator above acts on functions with arguments $x_1, ..., x_N$, $R_1, ..., R_M \in \mathbb{R}^3$. The argument x_i with $i \in \{1, ..., N\}$ is associated with the position of the i-th electron and R_j with $j \in \{1, ..., M\}$ is associated with the position of the j-th nucleus. To emphasise that the Laplace operators are defined with respect to different arguments, we denote by $\Delta_{x,l}$ the Laplace operator, acting on the i-th electron argument and by $\Delta_{R,j}$ the Laplace operator, acting on the j-th nucleus argument.

The nuclei of a molecule consist of neutrally charged neutrons with mass $M_{neu} = 1,7 \cdot 10^{-27} \ kg$ and positively charged protons $M_{pro} = 1,7 \cdot 10^{-27} \ kg$. The electron has a mass of $m_{ele} = 9,1 \cdot 10^{-31} \ kg$. Due to this mass difference the inertia of the nuclei is much larger than the inertia of the electrons. As the movement of the particles is based on coulomb interaction, which is identical for the affected particles, the electrons are much more accelerated than the nuclei. Hence, for a description of the electronic system, the position of the nuclei only enters as a fixed parameter. Therefore, the Hamilton operator Eq. (2.12) can be split into an electronic Hamilton operator and a nucleus Hamilton operator. For more details see [31, 32].

In this thesis, the focus is on the electronic Hamilton operator. For the sake of simplicity in equations, we consider the electronic Hamilton operator in atomic

units. This operator is given by:

$$(Hu)(x) = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i u(x) - \sum_{j=1}^{M} \frac{Z_j}{|x_i - R_j|} u(x) + \frac{1}{2} \sum_{j \neq i}^{N} \frac{1}{|x_i - x_j|} u(x) \right) \tag{2.13}$$
$$=: -\frac{1}{2}\Delta u(x) + V(x)u(x) \ .$$

2.3 Weak Formulation of the Electronic Schrödinger Equation

The starting point for the weak formulation of the electronic Schrödinger equation is a generalisation of the *Hardy inequality*.

Theorem 2.15. *Let $0 \leq 1 + \vartheta < 3/2$. Then*

$$\int \frac{1}{|x|^{2(1+\vartheta)}} u(x)^2 dx \leq c_H^2(\vartheta) |u|_{1+\vartheta}^2 \tag{2.14}$$

holds for all $u \in \mathcal{D}(\mathbb{R}^3)$ where

$$c_H(\vartheta) := \frac{2^{1-\vartheta}}{1+2\vartheta} \frac{\Gamma(1/4 - \vartheta/2)}{\Gamma(1/4 + \vartheta/2)} \tag{2.15}$$

is optimal. Here, Γ denotes the gamma function

$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt. \tag{2.16}$$

For a more detailed description of this equality and its proof see [33].
The kinetic part of the Hamilton operator does not cause a problem as the Laplace operator is easily described using the weak formulation. The potential V however, which in this case the coulomb potential, contains singularities. Therefore, one needs to show its square integrability. The results presented in the following are taken from [21]. We define the total nucleus charge of the molecule $Z := \sum_{i=1}^{M} Z_i$. Furthermore let

$$\theta(N, Z) := 3\sqrt{N} \max(N, Z) \ . \tag{2.17}$$

Using this definition we can state the following theorem:

Theorem 2.16. *Let $u, v \in \mathcal{D}(\mathbb{R}^{3N})$. Then*

$$\|Vu\|_{L^2(\mathbb{R}^{3N})} \leq \Theta(N, Z)|u|_{H^1(\mathbb{R}^{3N})} \ . \tag{2.18}$$

This theorem is a consequence of the Hardy inequality in Theorem 2.15 and Fubini's theorem. For a detailed proof see [21]. Using that $\mathcal{D}(\mathbb{R}^{3N})$ is dense in $H^1(\mathbb{R}^{3N})$ yields the following corollary.

Corollary 2.17. *Let $u \in H^1(\mathbb{R}^{3N})$. Then $x \mapsto (Vu)(x) = V(x)u(x)$ is square integrable, i.e. V can be interpreted as a multiplication operator from $H^1(\mathbb{R}^{3N})$ to $L^2(\mathbb{R}^{3N})$.*

Having established that the coulomb potential acting on a test function is square integrable, we can deduce the weak formulation of the electronic Schrödinger equation as follows: The Hamilton operator Eq. (2.13) induces a bilinear form $a : \mathcal{D}(\mathbb{R}^{3N}) \times \mathcal{D}(\mathbb{R}^{3N}) \to \mathbb{R}$ by

$$a(u,v) := \langle \nabla u, \nabla v \rangle_{(L^2(\mathbb{R}^{3N}))^{3N}} + \langle Vu, v \rangle_{L^2(\mathbb{R}^{3N})} . \tag{2.19}$$

Using Theorem 2.16 and the Cauchy-Schwarz inequality we find that

$$a(u,v) \leq (1 + \Theta(N,Z)) \|u\|_{H^1(\mathbb{R}^{3N})} \|v\|_{H^1(\mathbb{R}^{3N})} \tag{2.20}$$

for all $u, v \in \mathcal{D}(\mathbb{R}^{3N})$. Due the fact that $\mathcal{D}(\mathbb{R}^{3N})$ is a dense subspace of $H^1(\mathbb{R}^{3N})$ we can extend the bounded and symmetric bilinear form a on $\mathcal{D}(\mathbb{R}^{3N}) \times \mathcal{D}(\mathbb{R}^{3N})$ to a bounded and symmetric bilinear form on $H^1(\mathbb{R}^{3N}) \times H^1(\mathbb{R}^{3N})$.
The approach presented above does not take into account the spin as an extra parameter. Moreover, it does not respect Pauli's principle, i.e. fermionic state functions need to be anti-symmetric. Considering these further constraints on the domain of a we find that it is well defines on the H^1 subspace

$$\mathcal{V} := H^1\left(\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)^N\right) \cap \bigwedge_{i=1}^{N} L^2\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right) , \tag{2.21}$$

where $\wedge$ describes the antisymmetric tensor product of spaces, which guarantees Pauli's principle. Using this domain of a we further define the Schrödinger equation as a Rayleigh-Ritz variational principle

$$E_0 = \min_{\substack{\Psi \neq 0 \\ \Psi \in \mathcal{V}}} \frac{a(\Psi, \Psi)}{\langle \psi, \psi \rangle_{L^2}} \quad \text{and} \quad \psi_0 = \operatorname*{argmin}_{\substack{\Psi \neq 0 \\ \Psi \in \mathcal{V}}} \frac{a(\Psi, \Psi)}{\langle \psi, \psi \rangle_{L^2}} . \tag{2.22}$$

Due to the high dimensionality of the problem standard numerical approaches like the finite element method are not very promising as there is simply too much data to handle. To illustrate this we may consider a water molecule. Hydrogen possesses one electron and oxygen eight electrons. In the stationary case, without

consideration of spin and in the Born-Oppenheimer approximation the domain of the state function is $\mathbb{R}^{30}$. Discretising the unite square with 1000 data points in each direction yields 10^{90} function evaluation points. In comparison physicists estimate the number of particles in the universe to $\sim 10^{80}$ [34]. This exponential growth is also known as the curse of dimensionality.

Hence, further restriction to the model is needed to obtain a problem that can actually be simulated. This thesis shows several ways of doing this.

3 Hartree–Fock Method

In this section we present the basic idea of the *Hartree–Fock* method. Further, we give an introduction to the concept of *spin orbitals, Slater determinants* and *Excitation operators.* For a more detailed description of the Hartree–Fock method and the here presented concepts see [2, 35, 36].
We start by defining a discrete Galerkin Scheme to approximate the minimisation problem Eq. (2.22). Therefore, we reduce the N-particle problem Eq. (2.13) to N one particle problems. This is achieved by averaging the electron interaction. This *mean field approximation* is the basic idea of the *Hartree–Fock* method.
We write

$$H = \sum_{i=1}^{N} H_i \ , \tag{3.1}$$

where

$$H_i = \underbrace{-\frac{1}{2}\Delta_i^2 - \sum_{l=1}^{M} \frac{Z_l}{|r_i - R_l|}}_{=:h_i} + \frac{1}{2} \sum_{j=1,\ j\neq i}^{N} \underbrace{\frac{1}{|r_i - r_j|}}_{=:g(i,j)} \ . \tag{3.2}$$

Passing to the variational formulation the H_i describe the one particle problems:
Find $\varphi_i \in H^1\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)$ such that

$$
\begin{aligned}
a_i(\varphi_i, \varphi) := & -\frac{1}{2}\langle\nabla\varphi_i, \nabla\varphi\rangle - \sum_{l=1}^{M} \frac{Z_l}{|r_i - R_l|}\langle\varphi_i, \varphi\rangle + \frac{1}{2} \sum_{j=1,\ j\neq i}^{N} \frac{1}{|r_i - r_j|}\langle\varphi_i, \varphi\rangle \\
= & \ E_i\langle\varphi_i, \varphi\rangle
\end{aligned}
\tag{3.3}
$$

holds true for all $\varphi \in H^1\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)$. These N one particle eigenvalue problems yield solutions

$$\varphi_i : \mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\} \to \mathbb{C}; (x, s) \mapsto \varphi_i(x, s) \qquad , i \in \{1, ..., N\} \ , \tag{3.4}$$

which are defined as *spin orbitals*.

Definition 3.1. *A function* $\varphi_i \in H^1\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)$ *with*

$$\varphi_i : \mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\} \to \mathbb{C}; (x, s) \mapsto \varphi_i(x, s) \tag{3.5}$$

solving

$$a_i(\varphi_i, \varphi) = E_i \langle \varphi_i, \varphi \rangle \quad , \forall \varphi \in H^1 \left(\mathbb{R}^3 \times \left\{ \pm \frac{1}{2} \right\} \right) \tag{3.6}$$

is called **spin orbital**. *Two spin orbitals* φ_i *and* φ_j *are called* **orthonormal** *if*

$$\langle \varphi_i, \varphi_j \rangle := \sum_{s=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \varphi_i^*(x,s) \varphi_j(x,s) dx = \delta_{i,j} \tag{3.7}$$

holds true.

The product of spin orbitals is a mathematically possible solution, but leaves the set of physically possible states as it violates Pauli's principle stating that fermionic state functions have to be antisymmetric. This observation yields the idea to analyse the *antisymmetric* or *alternating product* of the spin orbitals. Indeed, the antisymmetric product of the spin orbitals guarantees the validity of Pauli's principle. The antisymmetric product of spin orbitals are called *Slater determinants* and are defined as follows.

Definition 3.2. *Be* $\{\varphi_1, ..., \varphi_N\}$ *a set of orthonormal spin orbitals. The function* Ψ_{SL} *defined by*

$$\Psi_{SL}[\nu_1, ..., \nu_N](x_1, s_1; x_2, s_2; ...; x_N, s_N) := \frac{1}{\sqrt{N!}} det \left[(\varphi_{\nu_i}(x_j, s_j))_{i,j=1}^N \right] \quad , \tag{3.8}$$

where ν_i *with* $i \in \{1, ..., N\}$ *are* N *non-identical indices, is called* **Slater determinant**. *We call the indices* **canonically ordered** *if* $\nu_i < \nu_{i+1}$ *for all* $i \in \{1, ..., N-1\}$.

With these Slater determinants we have a construction that can be used to define a discrete Galerkin scheme.
Subsequently we present the construction of the subspaces of $\mathcal{V}$ spanned by Slater determinants. Due to notational simplicity we set

$$\mathcal{X} := H^1 \left(\mathbb{R}^3 \times \left\{ \pm \frac{1}{2} \right\} \right) . \tag{3.9}$$

As the Slater determinant is an alternating form, we have to ensure that the spin orbitals are linearly independent, otherwise the Slater determinant is equal to zero. To obtain a mathematically clear definition of the relevant subspace, we define the space spanned by a set of spin orbitals.

Definition 3.3. *Be* $K \in \mathbb{N}$, $\{\varphi_1, ..., \varphi_K\}$ *a set of orthonormal spin orbitals and* $N \leq K$. *We define the* K-*dimensional subspace* $\mathcal{X}_K$ *of* $\mathcal{X}$ *by*

$$\mathcal{X}_K = span\{\varphi_i | i = 1, ..., K\} . \tag{3.10}$$

Remark 3.4. *To ensure convergence, we suppose the family* $\{\mathcal{X}_K\}_{K \in \mathbb{N}}$ *to be dense in* $L_2\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)$ *as well as in* $\mathcal{X}$.

Following we define the so called *full configuration interaction space* (FCI-space). This space is the relevant subspace for the discrete Galerkin scheme. As mentioned, we want to have a set of linearly independent spin orbitals for the construction of the Slater determinants. This is ensured by taking a basis set of $\mathcal{X}_K$. Supposing that $N \leq K$ with $N \in \mathbb{N}$, we can construct Slater determinants $\Psi_{SL}[\nu_1, ..., \nu_N]$ which is a generating set of the *full configuration interaction space.*

Definition 3.5. *Be* $K \in \mathbb{N}$, $\{\varphi_1, ..., \varphi_K\}$ *a set of orthonormal spin orbitals that form a basis of* $\mathcal{X}_K$ *and* $N \leq K$. *The* **full configuration interaction space** *is defined by*

$$\mathcal{V}_K := span\left\{\Psi_{SL}[\nu_1, ..., \nu_N]|\nu : \{1, ..., N\} \to \{1, ..., K\}\right.$$
$$\left.; i \mapsto \nu(i) = \nu_i \text{ and } \nu \text{ monotone}\right\} . \tag{3.11}$$

The additional assumption, that ν is monotone, is not necessary for the construction of the FCI-space. However, it does simplify the analysis of an orthonormal basis set and of dimensionality. For an orthonormal basis set the monotonicity of the indices assures that the Slater determinants given in the definition of the FCI-space form an orthonormal basis.

Lemma 3.6. *Be* $\nu_1 < \nu_2 < ... < \nu_N$ *a monotonically increasing selection of indices with* $1 \leq \nu_i \leq K$ *for all* $i \in \{1, ..., N\}$. *The Slater determinants built by spin orbitals* $\varphi_i \in \mathcal{X}_K$, $i \in \{1, ..., N\}$ *of the type* $\Psi_{SL}[\nu_1, ..., \nu_N]$ *form a complete orthonormal basis of* $\mathcal{V}_K$.

A proof of this lemma can be found in [2]. For the dimensionality we find the following asymptotic behaviour.

Lemma 3.7. *The dimension of* $\mathcal{V}_K$ *given by*

$$dim(\mathcal{V}_K) = \binom{K}{N} \sim \mathcal{O}(K^N) . \tag{3.12}$$

Proof. We see immediately that there are K over N options to define a monotone function from $\{1, ..., N\}$ to $\{1, ..., K\}$. Hence,

$$\dim(\mathcal{V}_K) = \binom{K}{N} = \frac{K!}{N!(K-N)!} = \frac{1}{N!}\frac{K(K-1)...(K-(N-1))(K-N)!}{(K-N)!}$$
$$= \prod_{i=1}^{N} \frac{K-N+i}{i} \leq \prod_{i=1}^{N} \frac{K-N+N}{1} = K^N .$$
$$\tag{3.13}$$

This proves the second claim that $dim(\mathcal{V}) \in \mathcal{O}\left(K^N\right)$ in K. $\qquad\square$

As mentioned, the FCI-space is used for the *Hartree–Fock* method and the full configuration interaction method (FCI method). Subsequently, we focus on the construction of the *Hartree–Fock method* before going into detail of the *full-CI method*.

The main reasons for which the *Hartree–Fock* method simplifies the calculation of a solution are the *Slater-Condon rules*. These seemingly easy rules, that have proven to be difficult to prove, reveal the structure of the overlap integrals of state functions with other state functions under the influence of the Hamilton operator. When defining the *Slater-Condon rules* in a mathematical framework, we have to start by defining the process of *physical excitation*. This is generally done by the so called *excitation operators*.

To build an N-electron Slater determinant one has to choose N non-identical indices $\nu_1, ..., \nu_N$ with the corresponding basis functions $\varphi_{\nu_i} \in \chi_K$ with $i \in \{1, ..., N\}$. By choosing these spin orbitals we divide the K spin orbitals into two groups, the *occupied* spin orbitals φ_{ν_i} with $i \in \{1, ..., N\}$ and the remaining $K - N$ *unoccupied* spin orbitals.

Definition 3.8. *Be $\{\varphi_1, ..., \varphi_K\}$ a set of orthonormal spin orbitals and $\nu_1, ..., \nu_N$ a set non-identical indices with $N \in \mathbb{N}$ and $N \leq K$. The spin orbitals $\{\varphi_{\nu_1}, ..., \varphi_{\nu_N}\}$ are called **occupied** and the remaining spin orbitals $\{\varphi_i | i \notin \{\nu_1, ..., \nu_N\}\}$ are called **unoccupied**.*

With *physical excitation* we refer to the process of *exciting* one electron from one of the occupied orbitals to one of the unoccupied orbitals. As this description makes use of fixed occupied and unoccupied spin orbitals, it is is defined in relation to a *reference Slater determinant* denoted by Ψ_0. Throughout this thesis Ψ_i^a denotes the state function where the occupied spin orbital φ_i is replaces by one of the unoccupied spin orbitals φ_a. Respectively, we define higher order excitations like *doubly excited* $\Psi_{i,j}^{a,b}$, *triply excited* $\Psi_{i,j,k}^{a,b,c}$ etc.. Subsequently we use a clearer notation by introducing a pair of index sequences denoted by Greek letters. To illustrate, we consider the excitation process from the occupied orbitals $(l_{\mu_1}, ..., l_{\mu_k})$ to the unoccupied orbitals $(a_{\mu_1}, ..., a_{\mu_k})$ with respect to the reference Slater determinant Ψ_0. We denote

$$\mu = \begin{pmatrix} a_{\mu_1}, ..., a_{\mu_k} \\ l_{\mu_1}, ..., l_{\mu_k} \end{pmatrix} . \tag{3.14}$$

This is a k-excitation, or an excitation of k*th* degree, where $k \leq N \leq K$. It is a common notation that the index set in canonical order of all possible k-excitations is denoted by $\mathcal{I}_k$, and the index set in canonical order of all possible excitations with respect to a reference Slater-determinant is denoted by $\mathcal{I}$. We denote the degree of the excitation by $\sharp\mu$ for $\mu \in \mathcal{I}$.

There are two things of momentous significance this notation. First, the capital,

calligraphic letters describe indices in canonical order. Therefore, we must introduce a phase factor to obtain a one to one relation between states in $\mathcal{V}_K$ and the excitation operators. Secondly, the physical excitation describes a change of occupied orbitals. Consequently, the reference Slater-determinant is not included in the set of Slater determinants described by the excitations defined by $\mathcal{I}$.

The mentioned phase factor of the state function which is given by ± 1 is a consequence of Pauli's principle. It can be illustrated by the previously introduced one excitation process:

We consider the reference Slater-determinant $\Psi[\nu_1, ..., \nu_{i-1}, \nu_i, \nu_{i+1}, ..., \nu_N]$. As the indices are in canonical ordering, $\nu_1 \leq ... \leq \nu_N$ holds true. Now, we consider the one excitation process where $\nu_a \leq \nu_1$. We find

$$\Psi_i^a := \Psi[\nu_1, ..., \nu_{i-1}, \nu_a, \nu_{i+1}, ..., \nu_N] = (-1)^{i-1}\Psi[\nu_a, \nu_1, ..., \nu_{i-1}, \nu_{i+1}, ..., \nu_N] . \tag{3.15}$$

This was a special example as we had to permute ν_a to the first position of the state describing indices to ensure the canonical ordering. In general, we have to permute every orbital into which was excited to the right position of the state describing indices. Due to notational simplicity we use the notation $(-1)^{p(\mu)}$ for the phase factor with respect to $\mu \in \mathcal{I}$. Using this setting we are able to define the excitation operator.

Definition 3.9. *For $\mu \in \mathcal{I}$ with $\sharp\mu = k$ and a given reference Slater-determinant Ψ_0 we define the excitation operator $X_\mu : \{\Psi_0\} \to \mathcal{V}_K$ by*

$$X_\mu \Psi_0 = \Psi_\mu = (-1)^{p(\mu)}\Psi_{l_{\mu_1}, ..., l_{\mu_k}}^{a_{\mu_1}, ..., a_{\mu_k}} \tag{3.16}$$

Remark 3.10. *The above construction can be extended to excitation operators defined on the space $\mathcal{V}_K$ instead of only the reference Slater-determinant. Here, $X_\mu\Psi = 0$ if X_μ excites out of an orbital that is not included in Ψ. Further, $X_\mu\Psi = 0$ if X_μ excites into an orbital that is already occupied in Ψ.*

The previous Remark 3.10 states a more general definition of the excitation operator which is used in the sequel.

With the excitation operators we defined a tool that allows us to compare degrees of excitation with respect to a reference Slater-determinant. The *Slater-Condon rules* state that the dual pairing of a single Slater-determinant with another single Slater-determinant under the operator H is zero unless the excitation degrees of the single Slater determinants obey some given structures. We emphasis that in the following theorem the excitation operators have the Slater-determinant they act on as their reference Slater-determinant.

Theorem 3.11 (Slater-Condon rules). *Let $\Psi^1_{SL}[\mu_1, ..., \mu_N]$ and $\Psi^2_{SL}[\nu_1, ..., \nu_N]$ be two Slater determinants built by the orbitals φ_{μ_i} and φ_{ν_i} with $i \in \{1, ..., N\}$. For the single particle operator $h = \sum_{i=1}^N h_i$ there hols*

$$
\begin{aligned}
\left\langle \Psi^1_{SL}, h\ \Psi^2_{SL} \right\rangle &= \sum_{i=1}^N \left\langle \varphi_{\mu_i}, h_{\mu_i}\ \varphi_{\mu_i} \right\rangle &&, \Psi^1_{SL} = \Psi^2_{SL} \\
\left\langle \Psi^1_{SL}, h\ \Psi^2_{SL} \right\rangle &= \left\langle \varphi_{\mu_i}, h_{\nu_j}\ \varphi_{\nu_j} \right\rangle &&, \Psi^2_{SL} = X^{\nu_j}_{\mu_i} \Psi^1_{SL} \\
\left\langle \Psi^1_{SL}, h\ \Psi^2_{SL} \right\rangle &= 0 &&, otherwise.
\end{aligned}
\tag{3.17}
$$

The two particle operator $g = \sum_{i=1}^N \sum_{j<i} g(i,j)$ satisfies

$$
\begin{aligned}
\left\langle \Psi^1_{SL}, G\ \Psi^2_{SL} \right\rangle &= \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \right\rangle &&, \Psi^1_{SL} = \Psi^2_{SL} \\
\left\langle \Psi^1_{SL}, G\ \Psi^2_{SL} \right\rangle &= \sum_{l=1}^N \left\langle \varphi_{\mu_i}, \varphi_{\mu_l} || \varphi_{\nu_j}, \varphi_{\mu_l} \right\rangle &&, \Psi^2_{SL} = X^{\nu_j}_{\mu_i} \Psi^1_{SL} \\
\left\langle \Psi^1_{SL}, G\ \Psi^2_{SL} \right\rangle &= \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\nu_a}, \varphi_{\mu_b} \right\rangle &&, \Psi^2_{SL} = X^{\nu_a, \nu_b}_{\mu_i, \mu_j} \Psi^1_{SL} \\
\left\langle \Psi^1_{SL}, G\ \Psi^2_{SL} \right\rangle &= 0 &&, otherwise.
\end{aligned}
\tag{3.18}
$$

In the above equation we have used the notation

$$
\left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\nu_a}, \varphi_{\mu_b} \right\rangle = \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\nu_a}, \varphi_{\mu_b} \right\rangle - \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\mu_b}, \varphi_{\nu_a} \right\rangle
\tag{3.19}
$$

where

$$
\left\langle \varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\nu_a}, \varphi_{\mu_b} \right\rangle = \sum_{s,s'=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\varphi^*_{\mu_i}(x,s) \varphi^*_{\mu_j}(x',s') \varphi_{\nu_a}(x,s) \varphi_{\mu_b}(x',s')}{|x-x'|}\ dx\ dx'
\tag{3.20}
$$

holds.

For a proof see [37].

Having the Slater-Condon rules we are able to start the derivation of the so called *Hartree–Fock* equations. By applying the Slater-Condon rules to the dual pairing defining the energy and find that

$$
E = \left\langle \Psi_{SL}, H\Psi_{SL} \right\rangle = \sum_{i=1}^N \left\langle \varphi_{\mu_i}, h_{\mu_i}\ \varphi_{\mu_i} \right\rangle + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \right\rangle
\tag{3.21}
$$

holds true. It is important to notice that in this formulation a single Slater-determinant Ψ_{SL} was in dual pairing. This is next to the mean-field approximation

the other main restriction of the *Hartree–Fock method*. The *Hartree–Fock theory* assumes that the solution of the discrete Galerkin scheme can be written as a single Slater-determinant. This shows that the solution of the respective minimisation problem, which we define in the following, can be formulated as an eigenvalue problem of the *Fock operator*. To be able to formulate this operator in a compact form we define the following auxiliary operators.

Definition 3.12. *Be $\{\varphi_1, ..., \varphi_N\}$ a set of orthonormal spin orbitals and $\Psi \in \mathcal{X}$. We define*

$$J_k(s, x)\Psi(s, x) = \sum_{s'=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \varphi_k^*(s', x') \frac{1}{|x - x'|} \varphi_k(s', x')\Psi(s, x)dx' \qquad (3.22)$$

and

$$K_k(s, x)\Psi(s, x) = \sum_{s'=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \varphi_k^*(s', x') \frac{1}{|x - x'|} \Psi(s', x')\varphi_k(s, x)dx' \; . \qquad (3.23)$$

*The operator J_k is the **Coulomb operator for the k-th spin orbital** and K_k is the **exchange operator for the k-th spin orbital**. Further we define*

$$J = \sum_{k=1}^{N} J_k \qquad (3.24)$$

and

$$K = \sum_{k=1}^{N} K_k \; , \qquad (3.25)$$

*the **Coulomb operator** and the **exchange operator**.*

Subsequently, we replace the different summands in Eq. (3.21) and start by analysing the second sum.

Lemma 3.13. *Be $\{\varphi_1, ..., \varphi_N\}$ a set of orthonormal spin orbitals. Then*

$$\sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_i, \varphi_j || \varphi_i, \varphi_j \rangle = \sum_{i=1}^{N} \langle \varphi_i, (J - K)\varphi_i \rangle \qquad (3.26)$$

holds true.

Proof. The main tool of this proof is Fubini's theorem. We start by expanding the considered terms by using their definition. We obtain

$$
\sum_{i=1}^{N}\sum_{j=1}^{N}\langle\varphi_i,\varphi_j||\varphi_i,\varphi_j\rangle
$$

$$
=\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{s,s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\varphi_i^*(x,s)\varphi_j^*(x',s')\varphi_i(x,s)\varphi_j(x',s')}{|x-x'|}\,dx\,dx'
$$

$$
-\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{s,s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\varphi_i^*(x,s)\varphi_j^*(x',s')\varphi_j(x,s)\varphi_i(x',s')}{|x-x'|}\,dx\,dx'\ .
$$

(3.27)

Using Fubinis theorem, and the definitions of the Coulomb operator for the i-th spin orbital and exchange operator for the i-th spin orbital we obtain

$$
\sum_{s,s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\varphi_i^*(x,s)\varphi_j^*(x',s')\varphi_i(x,s)\varphi_j(x',s')}{|x-x'|}\,dx\,dx'
$$

$$
=\sum_{s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\varphi_j^*(x',s')\sum_{s=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\frac{\varphi_i^*(x,s)\varphi_i(x,s)\varphi_j(x',s')}{|x-x'|}\,dx\,dx'
$$

$$
=\sum_{s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\varphi_j^*(x',s')J_i(x',s')\varphi_j(x',s')\,dx'
$$

$$
=\langle\varphi_j,J_i\varphi_j\rangle
$$

(3.28)

and

$$
\sum_{s,s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\varphi_i^*(x,s)\varphi_j^*(x',s')\varphi_j(x,s)\varphi_i(x',s')}{|x-x'|}\,dx\,dx'
$$

$$
=\sum_{s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\varphi_j^*(x',s')\sum_{s=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\frac{\varphi_i^*(x,s)\varphi_j(x,s)\varphi_i(x',s')}{|x-x'|}\,dx\,dx'
$$

$$
=\sum_{s'=\pm\frac{1}{2}}\int_{\mathbb{R}^3}\varphi_j^*(x',s')K_i(x',s')\varphi_j(x',s')\,dx'
$$

$$
=\langle\varphi_j,K_i\varphi_j\rangle\ .
$$

(3.29)

Inserting this into Eq. (3.27) yields

$$
\begin{aligned}
\sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_i, \varphi_j || \varphi_i, \varphi_j \rangle &= \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_j, J_i \varphi_j \rangle - \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_j, K_i \varphi_j \rangle \\
&= \sum_{j=1}^{N} \langle \varphi_j, J \varphi_j \rangle - \sum_{j=1}^{N} \langle \varphi_j, K \varphi_j \rangle = \sum_{i=1}^{N} \langle \varphi_i, (J - K)\varphi_i \rangle \ ,
\end{aligned}
\tag{3.30}
$$

which proves the claim. □

This lemma yields the following reformulation of Eq. (3.21):

Lemma 3.14. *Be $\{\varphi_1, ..., \varphi_N\}$ a set of orthonormal spin orbitals and $\Psi_{SL}[1, ..., N]$ the therewith defined Slater determinant. The energy $E^{(SL)}$ for the given Slater determinant $\Psi_{SL}[1, ..., N]$ can be expressed using the Coulomb and the exchange operator. The energy is then given by*

$$
E^{(SL)} = \sum_{i=1}^{N} \left\langle \varphi_i, h + \frac{1}{2}(J - K)\varphi_i \right\rangle
\tag{3.31}
$$

where $h = \sum_{i=1}^{N} h_i$.

Proof. By definition we know

$$
E = \langle \Psi_{SL}, H\Psi_{SL} \rangle = \sum_{i=1}^{N} \langle \varphi_i, h_i \, \varphi_i \rangle + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_i, \varphi_j || \varphi_i, \varphi_j \rangle \ .
\tag{3.32}
$$

Further we see that

$$
h\,\varphi_i = h_i\,\varphi_i
\tag{3.33}
$$

holds true for all $i \in \{1, ..., N\}$ by construction of h. This and the Lemma 3.13 yield

$$
\begin{aligned}
E &= \sum_{i=1}^{N} \langle \varphi_i, h\,\varphi_i \rangle + \frac{1}{2}\left(\sum_{j=1}^{N} \langle \varphi_j, J\varphi_j \rangle - \sum_{j=1}^{N} \langle \varphi_j, K\varphi_j \rangle \right) \\
&= \sum_{i=1}^{N} \left\langle \varphi_i, h + \frac{1}{2}(J - K)\varphi_i \right\rangle \ ,
\end{aligned}
\tag{3.34}
$$

which proves the claim. □

The energy $E^{(SL)}$ therefore depends on the choice of the Slater determinant. Minimising this functional leads to the *Hartree–Fock energy.*

Definition 3.15. *Be K, $N \in \mathbb{N}$ fixed, $\{\varphi_1, ..., \varphi_N\}$ a set of orthonormal spin orbitals. The infimum over the set of energies for given single Slater determinant $\Psi_{SL} \in \mathcal{V}_K$ is called the* **Hartree–Fock energy** $E_0^{(HF)}$. *We write*

$$E_0^{(HF)} = \inf_{\substack{\Psi_{SL} \in \mathcal{V}_K \\ ||\Psi_{SL}|| = 1}} \langle \Psi_{SL}, H \Psi_{SL} \rangle \ . \tag{3.35}$$

It is important to emphasise that the minimisation problem given in Definition 3.15 is over the set of single Slater determinants, which is a subspace of $\mathcal{V}_K$. Hence, the calculated eigenvalues are upper bounds to the solution on $\mathcal{V}_K$ and therewith also to the exact solution.

We now define the *Fock operator*, and show its connection to the minimisation problem Eq. (3.35).

Definition 3.16. *The operator*

$$F = h + J - K \tag{3.36}$$

is the **Fock operator**.

Remark 3.17. *In comparison to Lemma 3.14, the part of the coulomb and of the exchange operator enter the definition doubly.*

Following, we present the lemma that states the connection between the Hartree–Fock energy $E_0^{(HF)}$ and the Fock operator.

Lemma 3.18. *The Hartree–Fock energy $E_0^{(HF)}$ is given by*

$$E_0^{(HF)} = \langle \Psi_{HF}, H \Psi_{HF} \rangle \ , \tag{3.37}$$

with Ψ_{HF} the Hartree–Fock determinant defined by $\Psi_{SL}[1, ..., N]$ where the Eigenfunctions φ_i with $i \in \{1, ..., N\}$ of the Fock operator $\mathcal{F}$ are used as spin orbitals.

Proof. We use the Lagrange multipliers method to prove the claimed connection between $E_0^{(HF)}$ and the Fock operator. This ansatz states

$$0 = \delta E^{(SL)} - \sum_{i=1}^{N} \sum_{j=1}^{N} \tilde{\Lambda}_{i,j} \left(\langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} \rangle - \langle \varphi_{\mu_i}, \delta\varphi_{\mu_j} \rangle \right) \ , \tag{3.38}$$

where $\tilde{\Lambda}_{i,j}$ are the Lagrange multipliers. The variational derivative of $E^{(SL)}$ is given by

$$\delta E^{(SL)} = \sum_{i=1}^{N} \langle \delta\varphi_{\mu_i}, h_{\mu_i}\,\varphi_{\mu_i} \rangle + \sum_{i=1}^{N} \langle \varphi_{\mu_i}, h_{\mu_i}\,\delta\varphi_{\mu_i} \rangle$$

$$+ \frac{1}{2} \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \rangle + \frac{1}{2} \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_{\mu_i}, \delta\varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \rangle \quad (3.39)$$

$$+ \frac{1}{2} \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_{\mu_i}, \varphi_{\mu_j} || \delta\varphi_{\mu_i}, \varphi_{\mu_j} \rangle + \frac{1}{2} \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \delta\varphi_{\mu_j} \rangle \;.$$

Taking a closer look at the different parts we observe that

$$\langle \varphi_k, \varphi_l | \varphi_m, \varphi_n \rangle = \sum_{s,s'=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\varphi_k^*(x,s)\varphi_l^*(x',s')\varphi_m(x,s)\varphi_n(x',s')}{|x-x'|}\; dx\; dx'$$

$$= \sum_{s,s'=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\varphi_l^*(x,s)\varphi_k^*(x',s')\varphi_n(x,s)\varphi_m(x',s')}{|x-x'|}\; dx\; dx' \quad (3.40)$$

$$= \langle \varphi_l, \varphi_k | \varphi_n, \varphi_m \rangle$$

holds true. Using this observation we can further conclude

$$\sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \rangle + \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_{\mu_i}, \delta\varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \rangle$$

$$= \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\mu_i}, \varphi_{\mu_j} \rangle + \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_{\mu_i}, \delta\varphi_{\mu_j} | \varphi_{\mu_i}, \varphi_{\mu_j} \rangle$$

$$- \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\mu_j}, \varphi_{\mu_i} \rangle - \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \varphi_{\mu_i}, \delta\varphi_{\mu_j} | \varphi_{\mu_j}, \varphi_{\mu_i} \rangle$$

$$= \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\mu_i}, \varphi_{\mu_j} \rangle + \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_j}, \varphi_{\mu_i} | \varphi_{\mu_j}, \varphi_{\mu_i} \rangle \quad (3.41)$$

$$- \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\mu_j}, \varphi_{\mu_i} \rangle - \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_j}, \varphi_{\mu_i} | \varphi_{\mu_i}, \varphi_{\mu_j} \rangle$$

$$= 2\sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\mu_i}, \varphi_{\mu_j} \rangle - 2\sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} | \varphi_{\mu_j}, \varphi_{\mu_i} \rangle$$

$$= 2\sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \rangle \;.$$

Analogously, we find

$$
\sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \delta\varphi_{\mu_i}, \varphi_{\mu_j} \right\rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \delta\varphi_{\mu_j} \right\rangle
$$
$$
= 2 \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \delta\varphi_{\mu_i}, \varphi_{\mu_j} \right\rangle \; . \tag{3.42}
$$

This and the Lemma 3.14 yields

$$
\delta E^{SL} = \sum_{i=1}^{N} \left\langle \delta\varphi_{\mu_i}, h \; \varphi_{\mu_i} \right\rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} || \varphi_{\mu_i}, \varphi_{\mu_j} \right\rangle
$$
$$
+ \sum_{i=1}^{N} \left\langle \varphi_{\mu_i}, h \; \delta\varphi_{\mu_i} \right\rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_{\mu_i}, \varphi_{\mu_j} || \delta\varphi_{\mu_i}, \varphi_{\mu_j} \right\rangle \tag{3.43}
$$
$$
= \sum_{i=1}^{N} \left\langle \delta\varphi_{\mu_i}, F \; \varphi_{\mu_i} \right\rangle + \sum_{i=1}^{N} \left\langle \varphi_{\mu_i}, F \; \delta\varphi_{\mu_i} \right\rangle \; .
$$

Inserting this in Eq. (3.38), leads with $\tilde{\Lambda}_{i,j} = \tilde{\Lambda}_{j,i}^*$ and $\langle \varphi_{\mu_i}, \varphi_{\mu_j} \rangle = \langle \varphi_{\mu_j}, \varphi_{\mu_i} \rangle^*$ to the equation

$$
\sum_{i=1}^{N} \left(\left\langle \delta\varphi_{\mu_i}, F \; \varphi_{\mu_i} \right\rangle + \left\langle \varphi_{\mu_i}, F \; \delta\varphi_{\mu_i} \right\rangle - \sum_{j=1}^{N} \tilde{\Lambda}_{i,j} \left(\left\langle \delta\varphi_{\mu_i}, \varphi_{\mu_j} \right\rangle - \left\langle \varphi_{\mu_i}, \delta\varphi_{\mu_j} \right\rangle \right) \right)
$$
$$
= \sum_{i=1}^{N} \left\langle \delta\varphi_{\mu_i}, F \; \varphi_{\mu_i} - \sum_{j=1}^{N} \tilde{\Lambda}_{i,j} \varphi_{\mu_j} \right\rangle + \sum_{i=1}^{N} \left\langle \varphi_{\mu_i}, F \; \delta\varphi_{\mu_i} \right\rangle \tag{3.44}
$$
$$
+ \sum_{i=1}^{N} \sum_{j=1}^{N} \tilde{\Lambda}_{j,i} \langle \varphi_{\mu_j}, \delta\varphi_{\mu_i} \rangle
$$
$$
= 0 \; .
$$

Hence,

$$
F \; \varphi_{\mu_i} - \sum_{j=1}^{N} \tilde{\Lambda}_{i,j} \varphi_{\mu_j} = 0 \; . \tag{3.45}
$$

The solutions $\{\varphi_{\mu_j}\}_{j \in \{1,\dots,N\}} \subseteq \mathcal{V}_K$ can not be chosen freely, but have to form an orthonormal set. An obvious solution of Eq. (3.45) can be seen by choosing φ_{μ_i} as eigenfunctions of the Fock operator F with eigenvalues λ and $\tilde{\Lambda}_{i,j} = \lambda \delta_{j,i}$. This proves the claim. $\qquad \square$

These eigenvalue equation are also called the Hartree–Fock equations. The eigenfunctions corresponding to the N lowest eigenvalues form again a set of spin orbitals. Replacing the set of spin orbitals used to define the Fock operator with the newly calculated ones, and staring the eigenvalue calculations all over again implies a sequence of Hartree–Fock Energies.

The convergence of this sequence is not given trivially. As the focus of this work is on the analysis of the *coupled cluster* method we end the analysis of the Hartree–Fock method by presenting the following theorem.

Theorem 3.19. *We assume the molecule to be neutral or positively charged, i.e.* $N \leq Z := \sum_{k=1}^{M} z_k$. *Then*

i) *The Sequence of Hartree–Fock energies converges to a minimal Hatree fock limit and possesses a corresponding eigenstate $\Psi_0^{(HF)}$ defined by the N eigenfunctions $\phi_1^{(0)}, ..., \phi_N^{(0)}$. The respective eigenvalue is given by $\Lambda_0 = \sum_{i=1}^{N} \lambda_i$.*

ii) *For the eigenfunctions holds*

$$\phi_i^{(0)} \in H^2(\mathbb{R}^3 \times \{\pm 1/2\}) \cap \mathcal{C}^{0,1}(\mathbb{R}^3 \times \{\pm 1/2\}) \cap \mathcal{C}^{\infty}(\mathbb{R}^3 \setminus \{R_k\}_{k=1}^{M} \times \{\pm 1/2\})$$

which is known as elliptic regularity.

iii) *The Fock operator defined by the eigenfunctions $\phi_1^{(0)}, ..., \phi_N^{(0)}$ is a self-adjoint operator on $L^2(\mathbb{R}^3 \times \{\pm 1/2\})$ with domain $H^2(\mathbb{R}^3 \times \{\pm 1/2\})$ and is bounded from below.*

iv) *The Aufbau principle holds: $\lambda_1 \leq ... \leq \lambda_N < 0$ are the lowest N eigenvalues.*

For a more detailed description of the Hartree–Fock method and the above theorem see [38, 39, 40].

Before moving on to the *full configuration interaction* method, we introduce the *size consistency* of calculation methods used in quantum chemistry:

Definition 3.20. *Let A and B be two non-interacting systems. A given theory for the evaluation of the energy is called **size consistency** if the energy of the system $A + B$ is equal to the sum of the energy of A and the energy of B.*

$$E(A + B) = E(A) + E(B) \tag{3.46}$$

We want to end this section with the following theorem.

Theorem 3.21. *The Hartree–Fock method is size consistent*

Proof. Be A and B two non-interacting subsystems. The Hartree–Fock method for subsystem A yield $\Psi_{0,A}^{(HF)} = X_\mu^{(A)}\Psi_0$ satisfying

$$E_A^{(HF)} = \langle \Psi_{0,A}^{(HF)}, H_A \Psi_{0,A}^{(HF)} \rangle \ , \tag{3.47}$$

respectively for the subsystem B. We see that the product state of these solutions is a solution of the super-system as the systems do not interact, also implying that the solutions have zero overlap integral $\langle \Psi_{0,A}^{(HF)}, \Psi_{0,B}^{(HF)} \rangle = 0$. Further,

$$
\begin{aligned}
&\langle X_\mu^{(A)} X_\mu^{(B)} \Psi_0, (H_A + H_B) X_\mu^{(A)} X_\mu^{(B)} \Psi_0 \rangle \\
&= \langle X_\mu^{(A)} \Psi_0, (X_\mu^{(B)})^\dagger H_A X_\mu^{(A)} X_\mu^{(B)} \Psi_0 \rangle + \langle X_\mu^{(B)} \Psi_0, (X_\mu^{(A)})^\dagger H_B X_\mu^{(A)} X_\mu^{(B)} \Psi_0 \rangle \\
&= \langle X_\mu^{(A)} \Psi_0, H_A X_\mu^{(A)} \Psi_0 \rangle + \langle X_\mu^{(B)} \Psi_0, H_B X_\mu^{(B)} \Psi_0 \rangle \\
&= E_A^{(HF)} + E_B^{(HF)}
\end{aligned}
\tag{3.48}
$$

holds, which proves the claim. □

4 Full Configuration Interaction Method

Concepts like spin orbitals, Salter-determinants, etc., showed in the beginning of the previous chapter, yield a more precise method than the Hartree–Fock method, namely the *full configuration interaction method* (full-CI method). This section is geared to [2, 35].

In the previous chapter we introduced the full configuration interaction space $\mathcal{V}_K$ for given $K, N \in \mathbb{N}$ with $K > N$ as the span of all possible Slater determinants. Further, we have seen that the Hartree–Fock method minimises over the subspace of $\mathcal{V}_K$ consisting of single Slater determinants. Hence, the Hartree–Fock energy $E_0^{(HF)}$ was an upper bound to the solution of the minimisation problem over $\mathcal{V}_K$. In this section we analyse the method obtained by the minimisation over $\mathcal{V}_K$. The respective discrete Galerkin-Scheme is called *full configuration interaction method* and is defined as follows:

Definition 4.1. *Be $\mathcal{V}_K$ as above. We define the **full configuration interaction method** by*

$$E_0^{(FCI)} := min \left\{ \langle \psi, H\psi \rangle \mid \langle \psi, \psi \rangle = 1, \psi \in \mathcal{V}_K \right\} \tag{4.1}$$

and

$$\psi_{FCI} := argmin \left\{ \langle \psi, H\psi \rangle \mid \langle \psi, \psi \rangle = 1, \psi \in \mathcal{V}_K \right\} . \tag{4.2}$$

Remark 4.2. *We see immediately that*

$$E_0^{(HF)} \geq E_0^{(FCI)} \geq E_0 \tag{4.3}$$

holds by definition of the space $\mathcal{V}_K$ as subspace of $\mathcal{V}$.

We emphasise that the construction of $\mathcal{V}_K$ uses an arbitrary choice of spin orbitals. This is a very vast truncation of the basis of $\mathcal{V}$. Therefore, we mention the following theorem characterising the truncation error for the presented discrete Galerkin scheme.

Theorem 4.3. *Let E_0 be the lowest eigenvalue of H, having multiplicity one, together with a corresponding eigenfunction Ψ, normalised by $\langle \Psi, \Psi \rangle = 1$ and*

K_0 *sufficiently large. Then, for all $K > K_0$, there exist functions $\Psi_K \in \mathcal{V}_K$ corresponding to a single lowest eigenvalue $E_{0,K}$ solving the full-CI method*

$$E_{0,K} := \min \left\{ \langle \psi, H\psi \rangle \mid \langle \psi, \psi \rangle = 1, \psi \in \mathcal{V}_K \right\} \tag{4.4}$$

normalised as in

$$\Psi_K := argmin \left\{ \langle \psi, H\psi \rangle \mid \langle \psi, \psi \rangle = 1, \psi \in \mathcal{V}_K \right\} \tag{4.5}$$

which satisfies the following error bounds

$$||\Psi - \Psi_K||_{\mathcal{V}} \leq C \inf_{\Phi_K \in \mathcal{V}_K} ||\Psi - \Phi_K||_{\mathcal{V}} \tag{4.6}$$

and

$$0 \leq E_{0,K} - E_0 \leq C||\Psi - \Psi_K||_{\mathcal{V}}^2 . \tag{4.7}$$

For a proof of this theorem we refer to [21, 41].

The theorem above exposes the connection of the discrete Galerkin scheme and the full CI-method. Basically, we obtain all positive properties of the Galerkin scheme, implying that Ψ_K approximates Ψ quasi optimally. Furthermore, we have *super-convergence* of the eigenvalue. This means that it converges quadratically compared to the convergence of the eigenfunction. We must also emphasise that the calculated eigenvalue $E_{0,K}$ is non-degenerated under the condition that $\mathcal{V}_K$ is a sufficiently good approximation space. The sufficiently good property is guaranteed when setting $K > K_0$.

In the full configuration interaction ansatz we can deduce a general characterisation for any excited state $\Psi \in \mathcal{V}_K$. This representation is based on the fact that the full configuration interaction space is the span of Slater determinants. Hence, its elements are linearly parametrised. This is one of the mayor differences to the later presented *coupled cluster* approach, where the state functions are parametrised in a non-linear way. This characterisation is express in the following lemma.

Lemma 4.4. *Let $\Psi_0 = \Psi[1, ..., N] \in \mathcal{V}_K$ be a single-reference Slater determinant and $\Psi_1 \in \mathcal{V}_K$ be arbitrary satisfying the intermediate normalisation $\langle \Psi_0, \Psi_1 \rangle = 1$. Then there exists exactly one excitation operator of the form*

$$T = I + \sum_{\mu \in \mathcal{I}} c_\mu X_\mu \tag{4.8}$$

such that

$$\Psi_1 = \left(I + \sum_{\mu \in \mathcal{I}} c_\mu X_\mu \right) \Psi_0 \tag{4.9}$$

We denote these functions by Ψ_{CI}.

Proof. As $\mathcal{V}_K$ is defined as Span of possible N-electron Slater determinants, constructed with the basis set of $\mathcal{X}_K$, it is a linear space. Therefore, $\Psi_1 - \Psi_0 \in \mathcal{V}_K$ and by construction there exists a set of Slater determinants $\{\Psi_{SL}^{(s)}\}_{s \in \{1,...,\sharp\mathcal{I}\}}$ such that

$$\Psi_1 - \Psi_0 = \sum_{s \in \{1,...,\sharp\mathcal{I}\}} \alpha_s \Psi_{SL}^{(s)} \tag{4.10}$$

holds true. As seen in the previous chapter, there exists a one-to-one relation between Slater determinants and excitation operators. Thus, for every $\Psi_{SL}^{(s)}$ we find an excitation operator X_s such that

$$\Psi_{SL}^{(s)} = X_s \Psi_0 \ . \tag{4.11}$$

Inserting this into Eq. (4.10) and substituting $s \in \{1,...,\sharp\mathcal{I}\}$ by the respective $\mu \in \mathcal{I}$ yields the claim. $\qquad\square$

This characterisation shows that the minimisation problem in Definition 4.1 can be expressed as a minimisation problem over $\{c_\mu | \mu \in \mathcal{I}\}$. This version is more common in quantum chemistry. Consequently, we redefine the configuration interaction energy $E_0^{(CI)}$ with respect to the above presented characterisation of the state functions.

Definition 4.5. *The minimum of the expectation value of the Hamilton operator with respect to the linear expansion coefficients is called full configuration interaction energy* $E_0^{(FCI)}$

$$E_0^{(FCI)} = \min_{c_\mu \in \mathbb{R}^{\sharp\mathcal{I}}} \frac{\langle \Psi_{FCI}, H\Psi_{FCI} \rangle}{\langle \Psi_{FCI}, \Psi_{FCI} \rangle} \ . \tag{4.12}$$

This formulation is more common in quantum chemistry and computational physics as it shows that the minimisation can be obtained by solving the *projected Schrödinger equation*. From a mathematical point of view it helps to keep in mind that the full configuration method is nothing but a discrete Galerkin-Scheme. The *projected Schrödinger equation* is introduced in the following lemma.

Lemma 4.6. *For linear parametrised state functions* Ψ_{CI} *the minimisation*

$$E_0^{(FCI)} = \min_{c_\mu \in \mathbb{R}^{\sharp\mathcal{I}}} \frac{\langle \Psi_{FCI}, H\Psi_{FCI} \rangle}{\langle \Psi_{FCI}, \Psi_{FCI} \rangle} \tag{4.13}$$

is equivalent to solving the projected Schrödinger equations

$$\langle \Psi_\mu, H\Psi_{FCI} \rangle = E_0^{(FCI)} \langle \Psi_\mu, \Psi_{FCI} \rangle \tag{4.14}$$

for $\mu \in \mathcal{I}$.

Proof. We start by pointing out that

$$\frac{\partial}{\partial c_\mu} \Psi_{FCI} = \frac{\partial}{\partial c_\mu} \left(I + \sum_{\nu \in \mathcal{I}} c_\nu X_\nu \right) \Psi_0 = X_\mu \Psi_0 = \Psi_\mu \tag{4.15}$$

holds true. We define the function $h : \mathbb{R}^{\sharp\mathcal{I}} \to \mathbb{C}$ by

$$h(\{c_\mu\}) = \frac{\langle \Psi_{FCI}, H\Psi_{FCI} \rangle}{\langle \Psi_{FCI}, \Psi_{FCI} \rangle} \ , \tag{4.16}$$

with the partial derivatives

$$\begin{aligned}
\frac{\partial}{\partial c_\mu} h(\{c_\mu\}) &= \frac{\langle \Psi_\mu, H\Psi_{FCI} \rangle + \langle \Psi_{FCI}, H\Psi_\mu \rangle}{\langle \Psi_{FCI}, \Psi_{FCI} \rangle} \\
&\quad - \frac{\langle \Psi_{FCI}, H\Psi_{FCI} \rangle (\langle \Psi_\mu, \Psi_{CI} \rangle + \langle \Psi_{FCI}, \Psi_\mu \rangle)}{(\langle \Psi_{FCI}, \Psi_{FCI} \rangle)^2} \\
&= 2 \left(\frac{\langle \Psi_\mu, H\Psi_{FCI} \rangle \langle \Psi_{FCI}, \Psi_{FCI} \rangle - \langle \Psi_{FCI}, H\Psi_{FCI} \rangle \langle \Psi_\mu, \Psi_{FCI} \rangle}{(\langle \Psi_{FCI}, \Psi_{FCI} \rangle)^2} \right) .
\end{aligned}$$
$$\tag{4.17}$$

As h obtains its minimum in $\{\tilde{c}_\mu\} \in \mathbb{R}^{\sharp\mathcal{I}}$ where $h'(\{\tilde{c}_\mu\})v = 0$ with $v \in \mathbb{R}^{\sharp\mathcal{I}}$ this is equivalent to

$$0 = \langle \Psi_\mu, H\Psi_{FCI} \rangle \langle \Psi_{FCI}, \Psi_{FCI} \rangle - \langle \Psi_{FCI}, H\Psi_{FCI} \rangle \langle \Psi_\mu, \Psi_{FCI} \rangle$$
$$\Leftrightarrow \langle \Psi_\mu, H\Psi_{FCI} \rangle = E_{FCI} \langle \Psi_\mu, \Psi_{FCI} \rangle$$
$$\tag{4.18}$$

where we have used that $\langle \Psi_{FCI}, \Psi_{FCI} \rangle = 1$ and $\langle \Psi_{FCI}, H\Psi_{FCI} \rangle = E_0^{(FCI)}$. $\qquad\square$

Due to the linear parametrisation of the full configuration interaction method, the dimension scaling shown in Lemma 3.7 increases rapidly with the number of electrons. This makes this method numerically expensive in comparison to other methods. Its advantage however, to the Hartree–Fock method, is that it is not a *single-reference method*, meaning that the solution does not have to consist of one Slater determinant. This is the key to strongly correlated systems which means that the full configuration interaction method is the preferred method. Unfortunately, the bad scaling of the dimensions makes it extremely expensive.

In Lemma 4.4 we have seen that the full-CI method is based on a linear parametrisation of the state function. Truncating the set of linear combinations reduces the computational time. This is then called the *CI-method*. Even though the computational time becomes manageable one loses size consistency, one of the main properties of quantum chemical calculation method.

Theorem 4.7. *The full-CI-method is size consistent.*

Proof. We assume a system divided into two subsystems A and B with respective Hamilton operators H_A and H_B. Further, let Ψ_{FCI}^A and Ψ_{FCI}^B be the full-CI solutions in the respective subsystems. As the full-CI solution is not necessarily a single-reference solution, we can divide it into the Hartree–Fock solution (single-reference part) and the correlation term, which is not respected in the Hartree–Fock solution. Hence,

$$\Psi_{FCI}^A = T_A^{(FCI)}\Psi_0 = \left(T_A^{(HF)} + T_A^{(corr)}\right)\Psi_0 \ . \tag{4.19}$$

The operator $T_A^{(HF)}$ generates the Hartree–Fock solution $\Psi_{HF}^A = T_A^{(HF)}\Psi_0$ of the subsystem A. The operator $T_A^{(corr)}$ generates the correlation part of the state function. The full-CI solution Ψ_{FCI}^A fulfils by construction the equation

$$H_A\Psi_{FCI}^A = E_{0,A}^{(FCI)}\Psi_{FCI}^A \ . \tag{4.20}$$

Analogously to the full-CI state function we can divide the full-CI energy $E_{0,A}^{(FCI)}$. We find

$$
\begin{aligned}
E_{0,A}^{(FCI)} &= E_{0,A}^{(HF)} + E_{0,A}^{(corr)} \ , \\
E_{0,A}^{(HF)} &= \langle \Psi_{HF}^A, H_A\Psi_{HF}^A \rangle \ , \\
E_{0,A}^{(corr)} &= \frac{\langle \Psi_{FCI}^A, \left(H_A - E_{0,A}^{(HF)}\right)\Psi_{FCI}^A \rangle}{\langle \Psi_{FCI}^A, \Psi_{FCI}^A \rangle} \ .
\end{aligned} \tag{4.21}
$$

The results shown above were without loss of generality deduced for the subsystem A. Analogous equations hold for the subsystem B.

If we consider the subsystems to be infinitely far apart, thus interaction is negligible and we find

$$\Psi_{FCI}^{AB} = T_A^{(FCI)}T_B^{(FCI)}\Psi_0 \ . \tag{4.22}$$

This state function describes the size consistent solution for the super system

$$(H_A + H_B)\Psi_{FCI}^{AB} = (E_{0,A}^{(FCI)} + E_{0,B}^{(FCI)})\Psi_{FCI}^{AB} \ . \tag{4.23}$$

Expanding the state function Ψ_{FCI}^{AB} we find

$$
\begin{aligned}
\Psi_{FCI}^{AB} &= T_A^{(FCI)}T_B^{(FCI)}\Psi_0 \\
&= \left(T_A^{(HF)}T_B^{(HF)} + T_A^{(HF)}T_B^{(corr)} + T_A^{(corr)}T_B^{(HF)} + T_A^{(corr)}T_B^{(corr)}\right)\Psi_0
\end{aligned} \tag{4.24}
$$

and analogously for the energy

$$E_{0,AB}^{(FCI)} = E_{0,A}^{(HF)} + E_{0,B}^{(HF)} + E_{0,A}^{(corr)} + E_{0,B}^{(corr)} \ . \tag{4.25}$$

In Theorem 3.21 we have shown that the Hartree–Fock energy $E_{0,A}^{(HF)} + E_{0,B}^{(HF)}$ is size consistent. Hence, the correlation energy $E_{0,A}^{(corr)} + E_{0,B}^{(corr)}$ has to be size consistent too. This implies that the full-CI energy is size consistent which was the claim. $\square$

Even though the full-CI method has the desired property of being size consistent its truncated version, the CI-method, does not. Hence, the CI-method yields inaccurate dissociation energies. We conclude this chapter on the full configuration interaction method with the following remark.

Remark 4.8. *The CI-method is in general not size consistent. Consider for instance the CI-double method that only considers double excited correlation terms. We again divide the system into two subsystems A and B with respective Hamilton operators H_A and H_B. The CI-SD method yields the solutions $\Psi_{0,A}^{(CI)}$ and $\Psi_{0,B}^{(CI)}$ being described by excitation operators upto an excitation rank of two. The sum of these states is described by excitation operators upto an excitation rank of four. As the CI-SD method for the super system generates only excitation ranks upto doubly excitations the CI-SD is in general not size consistent.*

5 Single-Reference Coupled Cluster Method

In this chapter we introduce the *coupled cluster* formalism. The traditional *coupled cluster* method is a single-reference approach which distinguishes itself by not using a linear parametrisation in the Galerkin scheme, but a non-linear parametrisation. The characterisation of this non-linear parametrisation is presented in the first section on the *exponential ansatz*. Following, we present an analysis of the coupled cluster method. We have restricted our analysis to the *projected coupled cluster* method. There are many ways to characterise the *coupled cluster* method due to the fact that the non-linear parametrisation yields the method to be non-variational. We would like to mention that recent work has been done to describe and analyse the *coupled cluster* method in a variational way. This approach is called the *bi-variational* formulation. For more details on the *bi-variational* formulation and its application to the *coupled cluster* formalism see [6, 42, 43, 44, 45].

5.1 Exponential Ansatz

In Lemma 4.4 we have seen that the full CI-ansatz provides a linear parametrisation of the excitation operators. This has made it possible to reformulate the minimisation problem as a problem of solving several projected Schrödinger equations. The previously presented methods have been independent of each other. However, one may consider methods that use the Hartree–Fock limit as an initial guess, and try to correct correlation energy which got neglected by the mean-field approximation. These methods are called post-Hartree–Fock methods. One of the most accurate post-Hartree–Fock methods is the *coupled cluster* method.
We start this section by revealing some of the underlying structure of the excitation operator. The following lemma introduces calculation rules of the dual pairing of a function and a function under the excitation operator. These integrals play a main role in the later analysis of the *coupled cluster* method.
This section is geared to [2]. For similar discussions see also [35].

Lemma 5.1.
Let $\mu,\ \nu \in \mathcal{I}$. Then

   i) for $\sharp\mu > \sharp\nu$ the equation

$$\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle = 0 \tag{5.1}$$

   holds for all $\alpha \in \mathcal{I}$.

   ii) for $\sharp\mu < \sharp\nu$ there exists at most one $\alpha \in \mathcal{I}$ such that

$$\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \neq 0 \tag{5.2}$$

   holds.

For an arbitrary $\nu \in \mathcal{I}$ there holds

$$\sharp\{(\alpha,\mu) \in \mathcal{I} \times \mathcal{I} | \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \neq 0\} = \sum_{\alpha,\mu\in\mathcal{I}} |\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle| \leq 2^{2\sharp\nu} \leq 2^{2N}$$
$$=: C_N \ . \tag{5.3}$$

Proof.

i) The Slater determinants are by definition orthogonal. The operator X_α increases the excitation rank at least by one and only excites out of the reference determinant. This yields that Ψ_ν can not be linearly transformed to $X_\alpha \Psi_\mu$. Hence

$$\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle = 0 \qquad , \forall \alpha \in \mathcal{I} \ . \tag{5.4}$$

ii) Let $\mu,\ \nu \in \mathcal{I}$ be given by

$$\mu = \begin{pmatrix} a_{\mu_1}, & \cdots & , a_{\mu_{\sharp\mu}} \\ l_{\mu_1}, & \cdots & , l_{\mu_{\sharp\mu}} \end{pmatrix} \quad \text{and} \quad \nu = \begin{pmatrix} a_{\nu_1}, & \cdots & , a_{\nu_{\sharp\nu}} \\ l_{\nu_1}, & \cdots & , l_{\nu_{\sharp\nu}} \end{pmatrix} , \tag{5.5}$$

with $\sharp\nu > \sharp\mu$. The orthogonality of the Slater determinants and the fact that X_α increases the excitation rank at least by one and only excites out of the reference determinant yields that

$$\{a_{\mu_1}, \ldots, a_{\mu_{\sharp\mu}}\} \subseteq \{a_{\nu_1}, \ldots, a_{\nu_{\sharp\nu}}\} \tag{5.6}$$

and

$$\{l_{\mu_1}, \ldots, l_{\mu_{\sharp\mu}}\} \subseteq \{l_{\nu_1}, \ldots, l_{\nu_{\sharp\nu}}\} \tag{5.7}$$

are necessary conditions for

$$\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \neq 0 \ . \tag{5.8}$$

Hence, we can define

$$\{a_{\alpha 1}, \ldots, a_{\alpha \sharp \alpha}\} := \{a_{\mu_1}, \ldots, a_{\mu_{\sharp \mu}}\} \setminus \{a_{\nu_1}, \ldots, a_{\nu_{\sharp \nu}}\} \tag{5.9}$$

and

$$\{l_{\alpha 1}, \ldots, l_{\alpha \sharp \alpha}\} := \{l_{\mu_1}, \ldots, l_{\mu_{\sharp \mu}}\} \setminus \{l_{\nu_1}, \ldots, l_{\nu_{\sharp \nu}}\} \ . \tag{5.10}$$

It follows immediately that $\Psi_\nu = X_\alpha \Psi_\mu$ for some constant λ. This yields

$$\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \neq 0 \ . \tag{5.11}$$

Be $\nu \in \mathcal{I}$ an arbitrary index given by

$$\nu = \begin{pmatrix} a_{\nu_1}, & \cdots & , a_{\nu_{\sharp \nu}} \\ l_{\nu_1}, & \cdots & , l_{\nu_{\sharp \nu}} \end{pmatrix} \ . \tag{5.12}$$

The first equality follows by the orthogonality of the Slater determinants the necessary condition for

$$\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \neq 0 \tag{5.13}$$

derived in ii). It therefore remains to show for how many $\mu \in \mathcal{I}$ the construction in ii) is possible. With other words, how many disjoint decompositions exist for $\{a_{\nu_1}, \ldots, a_{\nu_{\sharp \nu}}\}$ and $\{l_{\nu_1}, \ldots, l_{\nu_{\sharp \nu}}\}$. For each set we find

$$L = \sum_{n=0}^{\sharp \nu} \binom{\sharp \nu}{n} = 2^{\sharp \nu} \tag{5.14}$$

possible disjoint decompositions. Hence it follows

$$\sharp \{(\alpha, \mu) \in \mathcal{I} \times \mathcal{I} | \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \neq 0\} = L^2 = 2^{2\sharp \nu} \leq 2^{2N}. \tag{5.15}$$

$\square$

We are now going to generalise the class of operators used in Lemma 4.4 to express any state in $\mathcal{V}_K$ by a sequence of excitation operators and a reference Slater-determinant.

Definition 5.2. *Be $N \leq K$ with $N, K \in \mathbb{N}$ and $\{\varphi_1, ..., \varphi_K\}$ an orthonormal basis of $\mathcal{X}_K$. For the excitation operators of an N-electron problem with respect to some reference Slater-determinant Ψ_0 we define the set*

$$\mathcal{L} = \left\{ t_0 I + T \ \middle| \ T = \sum_{\mu \in \mathcal{I}} t_\mu X_\mu \ and \ t_0, t_\mu \in \mathbb{C} \right\} \tag{5.16}$$

*as the **algebra of excitation operators***.

As we have seen in Lemma 4.4, this class of operators plays a central role for the description of excited states using a reference Slater determinant in the full configuration interaction ansatz. Subsequently, we see that it also plays a central role by describing the state functions on a non-linear manifold.

Before moving on to the characterisation of state functions on a non-linear mannifold, we show some algebraic and functional analytic results for the algebra of excitation operators. These are central in the characterisation of an excited state with a non-linear parametrisation in the Galerkin ansatz.

Lemma 5.3. *The operator class $\mathcal{L}$ forms a closed commutative sub-algebra in the algebra of linear operators $L(\mathcal{V}_K, \mathcal{V}_K)$. This algebra is closed under inversion and the spectrum of $L := I - T \in \mathcal{L}$ is $\sigma(L) = \{1\}$. Furthermore, the excitation operators T are nilpotent. It holds $T^k = 0$ for all $k > N$.*

Proof. We start by showing that the excitation operators commute. We choose $\mu = \begin{pmatrix} \alpha \\ i \end{pmatrix}$ und $\nu = \begin{pmatrix} \beta \\ j \end{pmatrix}$ where $i \neq j$ and $\alpha \neq \beta$. Due to simplicity of the notation we use the physical concept of *creation* and *annihilation operators* [46]. With this concept we can write the excitation operator as $X_\mu = a_\alpha^\dagger a_i$ and $X_\nu = a_\beta^\dagger a_j$. These *creation* and *annihilation operators* follow different commutator relations depending on weather they describe fermionic or bosonic particles [35, 46]. Using the commutator relation of fermionic *creation* and *annihilation operators*, we obtain

$$X_\mu X_\nu = a_\alpha^\dagger a_i a_\beta^\dagger a_j = a_\beta^\dagger a_\alpha^\dagger a_i a_j = a_\beta^\dagger a_j a_\alpha^\dagger a_i = X_\nu X_\mu \tag{5.17}$$

which yields

$$[X_\mu, X_\nu] = 0 \ . \tag{5.18}$$

We remark that the excitation rank is increased at least by one. We deduce that the composition of two excitation operators T_1 and T_2 is again an excitation operator. This implies that $\mathcal{L}$ is an algebra and as $\mathcal{L} \subseteq L(\mathcal{V}_K, \mathcal{V}_K)$ it is a sub-algebra of $L(\mathcal{V}_K, \mathcal{V}_K)$.

The operators $T = \sum_{\mu \in \mathcal{I}} t_\mu X_\mu$ with $t_\mu \in \mathbb{C}$ are nilpotent. This immediately follows from the definition of the excitation operators as we consider a system of N electrons. Therefore, $X_\mu^k = 0$ for all $k > N$ which implies $T^k = 0$ for all $k > N$. The operators T are not invertible in $\mathcal{L}$ as it is constructed only by excitation operators and can therefore not decrease the excitation rank. However, $T^k = 0$ for all $k > 0$. Hence, we can define

$$L^{-1} := \sum_{k=0}^{\infty} T^k = \sum_{k=0}^{N} T^k = I + \sum_{k=1}^{N} T^k \tag{5.19}$$

and find

$$LL^{-1} = (I - T) \sum_{k=0}^{N} T^k = I - T^{N+1} = I \ . \tag{5.20}$$

This shows that every operator $L \in \mathcal{L}$ is invertible and its inverse is contained in $\mathcal{L}$. $\qquad\square$

Having these algebraic results, we can show the main result that the theory of the *coupled cluster* method is based on: The characterisation of state function in $\mathcal{V}_K$ by using a non-linear parametrisation.

Theorem 5.4. *Let $\Psi_0 \in \mathcal{V}_K$ be the reference Slater determinant (a single Slater determinant e.g. the Hartree–Fock limit) and $\Psi \in \mathcal{V}_K$ satisfying the intermediate normalisation $\langle \Psi, \Psi_0 \rangle = 1$. Then there exists an operator $T \in \mathcal{L}$ of the form*

$$T = \sum_{i=1}^{N} T_i = \sum_{\mu \in \mathcal{I}} t_\mu X_\mu \ , \tag{5.21}$$

such that

$$\Psi = e^T \Psi_0 \ . \tag{5.22}$$

Proof. According to Lemma 4.4 there exists an excitation operator $C = \sum_{\mu \in \mathcal{I}} c_\mu X_\mu$ such that

$$\Psi = (I + C)\Psi_0 \ . \tag{5.23}$$

We define the operator $A := I + C$ and use Theorem 2.7 to define

$$T := \frac{1}{2\pi i} \int_\Gamma (zI - A)^{-1} \log(z) dz \ . \tag{5.24}$$

where Γ denotes a sufficiently small circle in the complex plain around $z_0 = 1$. By the Lemma 5.3 we know that $\sigma(A) = z_0$. Therefore, by the Cauchy–Dunford Theorem 2.7, the operator T can be interpreted as $T = \log(A)$. The logarithm is defined as the analytical function on $\mathbb{C} \setminus \{z \in \mathbb{C} | z \in \mathbb{R}, \ x \leq 0\}$. As

$$(zI - A)^{-1} = ((z - 1)I - C)^{-1} = (z - 1)^{-1} \left(I - \frac{1}{z - 1} C \right)^{-1} \tag{5.25}$$

holds true we deduce with Lemma 5.3 that $T \in \mathcal{L}$ and that T fulfils $\exp(T) = A$. To show that T has indeed the stated form of a finite series we expand the logarithm as the power series

$$T = \log(I + C) = \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k - 1} C^k = \sum_{k=1}^{N} \frac{(-1)^{k-1}}{k - 1} C^k \ . \tag{5.26}$$

In the last equation we have used that the excitation operators are nilpotent. Hence, T is indeed of the stated form with $e^T = A$. $\qquad\square$

The theorem above is the foundation of what is called the *exponential ansatz*. Before going into details of this ansatz, we explain one of the major differences to the full configuration interaction ansatz. We have seen in Lemma 4.6 that solving the minimisation problem is equivalent to solving the projected Schrödinger equation. We show that due to the non-linear parametrisation of the *coupled cluster* state manifold we obtain in a similar approach an intractable set of non-linear equations for the excitation amplitudes. To show this we use an alternative, but equivalent, description of excited states on a non-linear manifold.

Lemma 5.5. *Be $N \leq K$ with $N, K \in \mathbb{N}$ and $\{\varphi_1, ..., \varphi_K\}$ an orthonormal basis of $\mathcal{X}_K$. For the excitation operators of an N-electron problem with respect to some reference Slater-determinant Ψ_0 there holds*

$$\exp\left(\sum_{\mu \in \mathcal{I}} t_\mu X_\mu\right) \Psi_0 = \left(\prod_{\mu \in \mathcal{I}}(I + t_\mu X_\mu)\right)\Psi_0 . \qquad (5.27)$$

Proof. For any excitation operator X_μ there holds $X_\mu^2 = 0$. Therefore,

$$\exp(X_\mu) = I + X_\mu . \qquad (5.28)$$

With the previously shown commutation relation for the excitation operator we deduce

$$\exp\left(\sum_{\mu \in \mathcal{I}} t_\mu X_\mu\right) = \prod_{\mu \in \mathcal{I}}\exp(t_\mu X_\mu) = \prod_{\mu \in \mathcal{I}}(I + t_\mu X_\mu) , \qquad (5.29)$$

which was the claim. $\qquad\square$

The full-CI method is equivalent to solving a set of separated projected Schrödinger equations, one for each parameter. Using the non-linear parametrisation this is not possible any more. In the following remark, we show that an analogous approach yields a set of coupled projected Schrödinger equations.

Remark 5.6. *For non-linear parametrised state functions Ψ_{CC} the minimisation problem*

$$E_0^{(CC)} = \min_{\mu \in \mathcal{I}} \frac{\langle \Psi_{CC}, H\Psi_{CC}\rangle}{\langle \Psi_{CC}, \Psi_{CC}\rangle} \qquad (5.30)$$

is equivalent to solving the projected Schrödinger equations

$$\langle \Psi_\mu, \prod_{\nu \in \mathcal{I}}(I + t_\nu X_\nu^{-1})H\Psi_{CC}\rangle = E_0^{(CC)}\langle \Psi_\mu, \prod_{\nu \in \mathcal{I}}(I + t_\nu X_\nu^{-1})\Psi_{CC}\rangle . \qquad (5.31)$$

Proof. We start by calculating the partial derivatives with respect to t_μ. We find

$$\frac{\partial}{\partial t_\mu}\Psi_{CC} = \frac{\partial}{\partial t_\mu}\left(\prod_{\nu\in\mathcal{I}}(I + t_\nu X_\nu)\right)\Psi_0 = \left(\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu)\right)\Psi_\mu .\qquad(5.32)$$

Further, we define the auxiliary function h by

$$h(\{t_\mu\}) = \frac{\langle\Psi_{CC}, H\Psi_{CC}\rangle}{\langle\Psi_{CC}, \Psi_{CC}\rangle} ,\qquad(5.33)$$

with the partial derivatives

$$\begin{aligned}
&\frac{\partial}{\partial t_\mu}h(\{t_\mu\})\\
&= \frac{\langle\Psi_\mu\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu^{-1}), H\Psi_{CC}\rangle + \langle\Psi_{CC}, H\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu)\Psi_\mu\rangle}{\langle\Psi_{CC}, \Psi_{CC}\rangle}\\
&\quad - \frac{\langle\Psi_{CC}, H\Psi_{CC}\rangle\left(\langle\Psi_\mu\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu^{-1}), \Psi_{CC}\rangle + \langle\Psi_{CC}, \prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu)\Psi_\mu\rangle\right)}{\langle\Psi_{CC}, \Psi_{CC}\rangle^2}\\
&= 2\frac{\langle\Psi_\mu\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu^{-1}), H\Psi_{CC}\rangle\langle\Psi_{CC}, \Psi_{CC}\rangle}{\langle\Psi_{CC}, \Psi_{CC}\rangle^2}\\
&\quad - 2\frac{\langle\Psi_{CC}, H\Psi_{CC}\rangle\langle\Psi_\mu\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu^{-1}), \Psi_{CC}\rangle}{\langle\Psi_{CC}, \Psi_{CC}\rangle^2} .
\end{aligned}$$
$$(5.34)$$

Taking into account that h attains a minimum in $\{\tilde{t}_\mu\}$, where $h'(\{\tilde{t}_\mu\}) = 0$, we can deduce

$$\langle\Psi_\mu\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu^{-1}), H\Psi_{CC}\rangle = E_0^{(CC)}\langle\Psi_\mu\prod_{\nu\in\mathcal{I}\setminus\mu}(I + t_\nu X_\nu^{-1}), \Psi_{CC}\rangle ,\qquad(5.35)$$

where we have used that $\langle\Psi_{CC}, H\Psi_{CC}\rangle = E_0^{(CC)}$. $\qquad\square$

The variational minimisation of the coupled cluster energy is as we see an extremely difficult procedure and can only be done for small molecular systems. Therefore, we choose a different approach to calculate the coupled cluster wave function.

In the full configuration interaction, the equivalence of the variational solution and the solution of the projected Schrödinger equations holds. In analogy to this projected ansatz for the full-CI method, we define the *projected coupled cluster* approach. This approach uses the projected Schrödinger equations. Projecting the Schrödinger equation against Ψ_μ yields

$$\begin{cases}\langle\Psi_\mu, He^T\Psi_0\rangle = E_0^{(CC)}\langle\Psi_\mu, e^T\Psi_0\rangle ,\\ \langle\Psi_0, He^T\Psi_0\rangle = E_0^{(CC)} ,\end{cases}\qquad(5.36)$$

where the coupled cluster energy is obtained by projecting against the reference state Ψ_0, as we assume that the intermediate normalisation $\langle \Psi_0, \Psi_{CC} \rangle = 1$ holds. The equations (5.36) are called the *unlinked coupled cluster equations*, and can be used to define the projected coupled cluster method. However, we will use a different definition. Before rigorously defining the *projected coupled cluster* method we want to introduce the *linked coupled cluster equations* and want to analyse their relation to the unlinked coupled cluster equations. We introduce the Schrödinger equation with an effective, non-hermitian similarity transformed Hamilton operator

$$e^{-T}He^{T}\Psi_0 = E_0^{(CC)}\Psi_0 \ , \tag{5.37}$$

where we have multiplied the Schrödinger equation from the left by the operator e^{-T}. Projecting analogously to Eq. (5.36), we obtain the so called *linked coupled cluster equations*

$$\begin{cases} \langle \Psi_\mu, e^{-T}He^{T}\Psi_0 \rangle = 0 \\ \langle \Psi_0, e^{-T}He^{T}\Psi_0 \rangle = E_0^{(CC)} \ . \end{cases} \tag{5.38}$$

The following theorem shows how linked and unlinked coupled cluster equations are connected.

Theorem 5.7. *Be $\Psi_0 \in \mathcal{V}$ a reference state. Then*

$$\begin{cases} \langle \Psi_\mu, He^{T}\Psi_0 \rangle = E_0^{(CC)}\langle \Psi_\mu, e^{T}\Psi_0 \rangle & , \mu \in \mathcal{I} \\ \langle \Psi_0, He^{T}\Psi_0 \rangle = E_0^{(CC)} \end{cases} \tag{5.39}$$

is equivalent to

$$\begin{cases} \langle \Psi_\mu, e^{-T}He^{T}\Psi_0 \rangle = 0 & , \mu \in \mathcal{I} \\ \langle \Psi_0, e^{-T}He^{T}\Psi_0 \rangle = E_0^{(CC)} \ . \end{cases} \tag{5.40}$$

In other words, linked and unlinked coupled cluster equations are equivalent if we have access to the full coupled cluster wave function.

Proof. This is an immediate consequence. Using that $\mathcal{V}$ is a Hilbert space the Riesz-map $\mathcal{R}$ is well-defined. Then, for any choice $\Psi_0 \in \mathcal{V}$ we find $\mathcal{R}(\Psi_0) \circ \exp(-T) = \mathcal{R}(\Psi_0)$ which yields

$$\langle \Psi_0, He^{T}\Psi_0 \rangle = \langle \Psi_0, e^{-T}He^{T}\Psi_0 \rangle = E_0^{(CC)} \ . \tag{5.41}$$

Using the orthogonality we can further deduce

$$\begin{aligned} 0 = \langle \Psi_\mu, e^{-T}He^{T}\Psi_0 \rangle &= \langle \Psi_\mu, (e^{-T} \pm I)He^{T}\Psi_0 \rangle \\ &= \langle \Psi_\mu, He^{T}\Psi_0 \rangle + \langle \Psi_\mu, (e^{-T} - I)He^{T}\Psi_0 \rangle \\ &= \langle \Psi_\mu, He^{T}\Psi_0 \rangle + E_0^{(CC)}\langle \Psi_\mu, e^{T}\Psi_0 \rangle \end{aligned} \tag{5.42}$$

$\square$

We emphasise that the in Theorem 5.7 shown equivalence does not imply that linked and unlinked coupled cluster equations are always equivalent. We will see that in the *truncated case*, this equivalence is more difficult to show, and for the *tailored coupled cluster approach* this equivalence is in general false.

5.2 Analysis of the Projected Coupled Cluster Method

We now come to the mathematical analysis of the *projected coupled cluster* method. This section is geared to [2]. We emphasise that there exists a more general mathematical framework for the coupled cluster method, the *continuous coupled cluster* formulation [47], and a respective analysis of it [48]. However, the main result of this thesis is the later analysis of the *tailored coupled cluster* method, where we make extensive use the here presented analysis.

The main tool that we have used in this section, and in the next chapter is the following *local version of Zarantonellos's theorem*. Therefore, we start this section by recalling this theorem.

Theorem 5.8 (Local Version of Zarantonellos's Theorem).
Let $f : X \to X'$ be a map between a Hilbert space $(X, \langle \cdot, \cdot \rangle, \| \cdot \|)$ and its dual X', and let $x_* \in B_\delta$ be a root, $f(x_*) = 0$, where B_δ is an open ball of radius δ around x_*.
Assume that f is Lipschitz continuous in B_δ, i.e. for all $x_1, x_2 \in B_\delta$ holds

$$\|f(x_1) - f(x_2)\|_{X'} \leq L\|x_1 - x_2\| \tag{5.43}$$

for a constant $L \geq 0$. Be further f locally strongly monotone in B_δ, i.e. for all $x_1, x_2 \in B_\delta$ holds

$$\langle f(x_1) - f(x_2), x_1 - x_2 \rangle \geq \gamma \|x_1 - x_2\|^2 \tag{5.44}$$

for some constant $\gamma > 0$. Then holds

i) The root x_* i unique in B_δ. Indeed, there is a ball $C_\varepsilon \subset X'$ with $0 \in C_\varepsilon$ such that the solution map $f^{-1} : C_\varepsilon \to X$ exists and is Lipschitz continuous, implying that the equation

$$f(x_* + x) = y \tag{5.45}$$

has a unique solution $x = f^{-1}(y) - x_*$, depending continuously on y, with norm $\|x\|_X \leq \delta$.

ii) *Moreover, let $X_d \subset X$ be a closed subspace such that x_* can be approximated sufficiently well, i.e. the distance $d(x_*, X_d)$ is small. Then, the projected problem $f_d(x_d) = 0$ has a unique solution $x_d \in X_d \cap B_\delta$, and*

$$\|x_* - x_d\| \leq \frac{L}{\gamma} d(x_*, X_d) . \tag{5.46}$$

Proof. As X is a Hilbert space, we recall that there exists a linear and bijective operator $\iota : X' \to X$. The proof of $i)$ is based on Banach's fixpoint theorem. For a given $x_0 \in B_\delta$ and $\tau > 0$ we define a sequence $(x_n)_{n \in \mathbb{N}} \subset X$ satisfying

$$\frac{1}{\tau}(x_{n+1} - x_n) + \iota f(x_n) = 0_X , \tag{5.47}$$

where 0_X denotes the zero element in X. The convergence of this sequence follows from Banach's fixpoint theorem applied to the map

$$\Phi : X \to X; x \mapsto x + \tau \iota (0_{X'} - f(x)) . \tag{5.48}$$

Due to the strong monotonicity and the Lipschitz continuity of f we find

$$\begin{aligned}
\|\Phi(v) - \Phi(w)\|^2 &= \|v - w - \tau \iota (f(v) - f(w))\|^2 \\
&= \|v - w\|^2 - 2\tau \langle \iota(f(v) - f(w)), v - w \rangle + \tau^2 \|\iota(f(v) - f(w))\|^2 \\
&\underset{(*)}{=} \|v - w\|^2 - 2\tau \langle f(v) - f(w), v - w \rangle + \tau^2 \|f(v) - f(w)\|_{X'}^2 \\
&\leq \|v - w\|^2 - 2\tau\gamma \|v - w\|^2 + \tau^2 L^2 \|v - w\|^2 \\
&= (1 - 2\tau\gamma + \tau^2 L^2) \|v - w\|^2 .
\end{aligned} \tag{5.49}$$

Be $0 < \tau < 2\gamma/L^2$ then Φ is a contraction. Hence, it follows the convergence of the sequence $(x_n)_{n \in \mathbb{N}}$ and therewith $i)$.

The existence and uniqueness of $x_* \in X$ and $x_d \in X_d$ follows from $i)$. Let $u_d \in X_d$ be arbitrarily chosen. Then

$$\langle f(x_*) - f(x_d), u_d \rangle = 0 \tag{5.50}$$

holds. By using the strong monotonicity and the Lipschitz continuity of f we find

$$\begin{aligned}
\gamma \|x_* - x_d\|^2 &\leq \langle f(x_*) - f(x_d), x_* - x_d \rangle = \langle f(x_*) - f(x_d), x_* - u_d \rangle \\
&\leq \|f(x_*) - f(x_d)\|_{X'} \|x_* - u_d\| \leq L \|x_* - x_d\| \|x_* - u_d\|
\end{aligned} \tag{5.51}$$

which proves $ii)$. $\qquad \square$

Having introduced the main theorem, we define the *projected couplde cluster* method in a purposeful way for this thesis.

Definition 5.9. *Be K, $N \in \mathbb{N}$ with $K > N$ fixed, $\{\varphi_1, ..., \varphi_K\}$ a set of orthonormal spin orbitals and Ψ_0 an N electron reference state. We define for the cluster amplitudes $t = (t_\nu)_{\nu \in \mathcal{I}}$ the **projected coupled cluster function** f by*

$$f : \mathbb{R}^{\sharp \mathcal{I}} \to \left(\mathbb{R}^{\sharp \mathcal{I}}\right)' ; t \mapsto (f_\mu(t))_{\mu \in \mathcal{I}} \tag{5.52}$$

where

$$f_\mu(t) = \langle \Psi_\mu, e^{-T} H e^T \Psi_0 \rangle = \langle \Psi_\mu, \exp(-\sum_{\nu \in \mathcal{I}} t_\nu X_\nu) H \exp(\sum_{\nu \in \mathcal{I}} t_\nu X_\nu) \Psi_0 , \tag{5.53}$$

*for $\mu \in \mathcal{I}$. We call $V := \mathbb{R}^{\sharp \mathcal{I}}$ the **space of cluster amplitudes**.*

Remark 5.10.

   i) Due to simplicity and the fact that there exists a one to one relation between cluster amplitudes and cluster operators, we use capital letters for the cluster operators corresponding to the cluster amplitudes denoted by small letters.

   ii) We see that the linked coupled cluster equations (5.38) can be formulated as

$$f(t) = 0 \tag{5.54}$$

   or

$$\langle v, f(t) \rangle = 0 \quad , \forall \ v \in V \tag{5.55}$$

Subsequently, we focus on proving that the projected coupled cluster function fulfils all requirements for the local version of Zarantonellos's theorem.
We start with two lemmas that are useful tools for several proofs throughout this and the following chapter.

Lemma 5.11. *Let F be the Fock operator and $X_\mu = X_{l_1,...,l_k}^{a_1,...,a_k}$. Then the following commutator can be computed explicitly*

$$[F, X_\mu] = [F, X_{l_1,...,l_k}^{a_1,...,a_k}] = \sum_{j=1}^{k} (\lambda_{a_j} - \lambda_{l_j}) X_\mu =: \varepsilon_\mu X_\mu . \tag{5.56}$$

Remark 5.12. *A direct consequence of this lemma is that the commutator of the Fock operator F and a cluster operator T can be computed explicitly by*

$$[F, T] = \sum_{\mu \in \mathcal{I}} \varepsilon_\mu t_\mu X_\mu . \tag{5.57}$$

Lemma 5.13. *For the Fock operator F and a given cluster operator T the Baker-Campbell-Hausdorff expansion can be computed explicitly and is given by*

$$e^{-T}Fe^{T} = F + [F, T] \ . \tag{5.58}$$

For the proofs of these lemmas we refer to [35].

We are now going to analyse how the norm of the cluster amplitude stands in relation with the norm of the state function, generated by the corresponding cluster operator acting on the reference Slater determinant.

Definition 5.14. *The map*

$$\| \cdot \|_V : V \to \mathbb{R}; t \mapsto \|t\|_V = \sqrt{\sum_{\mu \in \mathcal{I}} \varepsilon_\mu |t_\mu|^2} \tag{5.59}$$

*is called the **cluster amplitude norm**.*

Remark 5.15. *We see immediately that $\| \cdot \|_V$ is a norm if $\varepsilon_\mu \neq 0$. This is guaranteed by assuming a HOMO-LUMO gap.*

Having defined the normed space $(V, \|\cdot\|_V)$, we find the following norm equivalence under the assumption of a HOMO-LUMO gap, a gap between λ_N and λ_{N+1}. The existence of a HOMO-LUMO gap is equivalent to the assumption that the Nth and $(N+1)$th state are non-degenerate. From now on, we assume the existence of such a HOMO-LUMO gap.

Theorem 5.16. *For $t \in V$ and $T := \sum_{\mu \in \mathcal{I}} t_\mu X_\mu$ there holds*

$$\|t\|_V^2 = \langle T\Psi_0, e^{-T}Fe^{T} \rangle \sim \|T\Psi_0\|_{H^1}^2 \ . \tag{5.60}$$

Proof. Let Ψ_0 be the eigenfunction corresponding to the lowest eigenvalue Λ_0 of the Fock operator $F : \mathcal{V}_K \to \mathcal{V}'_K$. Since $e^{-T}Fe^{T} = F + [F, T]$ according to Lemma 5.13 we can use Lemma 5.11 and find that

$$\langle \phi, e^{-T}Fe^{T}\Psi_0 \rangle = \langle \phi, (F + [F, T])\Psi_0 \rangle = \langle \phi, \Lambda_0 \Psi_0 + \sum_{\mu \in \mathcal{I}} \varepsilon_\mu t_\mu \Psi_\mu \rangle \tag{5.61}$$

holds true for all $\phi \in \mathcal{V}_K$. Choosing $\phi = T\Psi_0$ yields

$$\langle T\Psi_0, (F + [F, T])\Psi_0 \rangle = \sum_{\mu \in \mathcal{I}} \varepsilon_\mu |t_\mu|^2 = \|t\|_V^2 \ . \tag{5.62}$$

For $\mu = \begin{pmatrix} a_1, ..., a_k \\ l_1, ..., l_k \end{pmatrix} \in \mathcal{I}$, the $\varepsilon_\mu = \sum_{i=1}^{k} \lambda_{a_i} - \lambda_{l_i}$ are bounded from below by the HOMO-LUMO gap

$$0 < \varepsilon_0 := \lambda_{N+1} - \lambda_N \leq \varepsilon_\mu \ . \tag{5.63}$$

We can therefore conclude that the spectrum of the matrix $(\langle \Psi_\mu, (F - \Lambda_0)\Psi_\nu \rangle)_{\mu,\nu \in \mathcal{I}}$ is bounded from below by ε_0. Considering that the Fock operator is an operator $F : H^1 \to H^1$ this implies that

$$\|\phi\|_{H^1}^2 \sim \langle \phi, (F - \Lambda_0)\phi \rangle \tag{5.64}$$

holds for all $\phi \in \mathcal{V}_K$ and $\phi \perp \Psi_0$. Choosing again $\phi = T\Psi_0$ yields

$$\begin{aligned}
\|T\Psi_0\|_{H^1}^2 &\sim \langle T\Psi_0, (F - \Lambda_0)T\Psi_0 \rangle = \langle T\Psi_0, FT\Psi_0 - TF\Psi_0 \rangle \\
&= \langle T\Psi_0, [F, T]\Psi_0 \rangle = \langle T\Psi_0, F + [F, T]\Psi_0 \rangle = \sum_{\mu \in \mathcal{I}} \varepsilon_\mu |t_\mu|^2 \\
&= \|t\|_V^2 \ ,
\end{aligned} \tag{5.65}$$

which shows the claim. $\qquad \square$

The above theorem states that the norm of a state function generated by the cluster operator T can be expressed by using the norm of the cluster amplitudes. An important remark on how the constants involved in this estimation depend on the number of spin orbitals K was presented in [2]. Here, it was shown that for uniform bounds one needs to assume:

  i) There exists a constant $C > 0$ such that $\|\Psi_0^{(HF)}\|_{H^1} \leq C$ holds for all $K \in \mathbb{N}$.

  ii) There exists a constant $C > 0$ such that $\|F_K\Psi\|_{H^{-1}} \leq C\|\Psi\|_{H^1}$ holds for all $\Psi \in \mathcal{V}_K$ and all $K \in \mathbb{N}$.

  iii) There exists a constant $C > 0$ such that $\lambda_{N+1} - \lambda_N > C$.

We leave this statement without proof as we are not able to show similar assumptions for the *tailored coupled cluster* method. Having established an equivalent measure for the state function, we continue to establish an equivalence with the operator norm. This yields statements about the boundedness of the cluster operator T. To establish such an equivalence we need the following lemma.

Lemma 5.17. *Be* $\alpha, \mu, \nu \in \mathcal{I}$ *with* $\sharp\alpha, \sharp\mu \leq \sharp\nu$ *and* $\alpha \oplus \mu = \nu$ *such that* $\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \neq 0$, *then there exists a constant* $C > 0$ *such that*

$$\frac{\varepsilon_\nu}{\varepsilon_\mu} \leq C\varepsilon_\alpha \ . \tag{5.66}$$

Proof. For the HOMO-LUMO gap $0 < \varepsilon_0 := \lambda_{N+1} - \lambda_N$ holds that $\varepsilon_\nu \geq \varepsilon_0$ and equivalently $\varepsilon_\nu^{-1} \leq \varepsilon_0^{-1}$ for all $\nu \in \mathcal{I}$. For $\nu = \begin{pmatrix} a_1, ..., a_k \\ l_1, ..., l_k \end{pmatrix} \in \mathcal{I}$ we define

$$\overline{\lambda}_\nu := \max_{i \in \{1,...,\sharp\nu\}} \{\lambda_{a_i}\} - \delta \,, \tag{5.67}$$

where $\delta := (\lambda_{N+1} + \lambda_N)/2$. As $\max_{i \in \{1,...,\sharp\nu\}}\{\lambda_{a_i}\} \geq \lambda_{N+1}$ we know that $\overline{\lambda}_\nu > 0$. We further remark that $\varepsilon_\nu \leq N(\overline{\lambda}_\nu - (\lambda_1 - \delta))$ and $\overline{\lambda}_\nu \geq \varepsilon_0/2$. Using these estimates we find

$$|\lambda_1 - \delta| = \frac{2\overline{\lambda}_\nu}{2\overline{\lambda}_\nu}|\lambda_1 - \delta| \leq \frac{2\overline{\lambda}_\nu}{\varepsilon_0}|\lambda_1 - \delta| \tag{5.68}$$

and therewith

$$\varepsilon_\nu \leq N(\overline{\lambda}_\nu + |\lambda_1 - \delta|) \leq \underbrace{N\left(1 + \frac{2|\lambda_1 - \delta|}{\varepsilon_0}\right)}_{C:=}\overline{\lambda}_\nu \,. \tag{5.69}$$

Hence, $C^{-1}\varepsilon_\nu \leq \overline{\lambda}_\nu \leq \varepsilon_\nu$. Since $\Psi_\nu = X_\alpha\Psi_\mu$ we consider two cases:

i) Be $\overline{\lambda}_\alpha \geq \overline{\lambda}_\mu$. Then $\overline{\lambda}_\alpha = \overline{\lambda}_\nu$ and therefore

$$\frac{\varepsilon_\nu}{\varepsilon_\mu} \leq \frac{C\overline{\lambda}_\nu}{\varepsilon_0} \leq \frac{C}{\varepsilon_0}\overline{\lambda}_\alpha \leq \frac{C}{\varepsilon_0}\varepsilon_\alpha \,. \tag{5.70}$$

ii) Be $\overline{\lambda}_\alpha \leq \overline{\lambda}_\mu$. Then $\overline{\lambda}_\mu = \overline{\lambda}_\nu$ and therefore

$$\frac{\varepsilon_\nu}{\varepsilon_\mu} \leq \frac{C\overline{\lambda}_\nu}{\overline{\lambda}_\mu} = C = C\frac{2\overline{\lambda}_\alpha}{2\overline{\lambda}_\alpha} \leq \frac{2C}{\varepsilon_0}\varepsilon_\alpha \,, \tag{5.71}$$

which shows the claim. $\qquad\square$

Having proven this lemma we, move on to the proof of the norm equivalence of the cluster operator norm in H^1 and the cluster amplitude norm in V.

Theorem 5.18. *For $t \in V$, the operator $T := \sum_{\mu \in \mathcal{I}} t_\mu X_\mu$ satisfies the estimate*

$$\|T\Psi\|_{H^1} \leq G\|t\|_V\|\Psi\|_{H^1} \tag{5.72}$$

for all $\Psi \in \mathcal{V}_K$ with $G > 0$. Moreover, the operator norm of the cluster operator $T : H^1 \to H^1$ is equivalent to $\|t\|_V$, we write:

$$\|T\|_{H^1 \to H^1} \sim \|t\|_V \,. \tag{5.73}$$

Proof. Be $\Psi = \sum_{\mu \in \mathcal{I}} c_\mu \Psi_\mu \in \mathcal{V}_K$ and $T = \sum_{\alpha \in \mathcal{I}} t_\alpha X_\alpha$. We further denote $\mathbf{c} = (c_\mu)_{\mu \in \mathcal{I}}$. According to Theorem 5.16 we find

$$\|T\Psi\|_{H^1}^2 \sim \|(\langle \Psi_\nu, T\Psi \rangle)_{\nu \in \mathcal{I}}\|_V^2 = \sum_{\nu \in \mathcal{I}} \left(\varepsilon_\nu^{1/2} | \sum_{\alpha, \mu \in \mathcal{I}} t_\alpha c_\mu \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle |^2 \right) . \quad (5.74)$$

Defining $D := diag(\varepsilon_\mu^{1/2})_{\mu \in \mathcal{I}}$ and $A = (\langle \Psi_\nu, T\Psi_\mu \rangle)_{\nu, \mu \in \mathcal{I}}$ we find

$$\|T\Psi\|_{H^1}^2 \sim \|DAD^{-1}D\mathbf{c}\|_{l_2}^2 \leq \|DAD^{-1}\|_{l_2 \to l_2}^2 \|D\mathbf{c}\|_{l_2}^2 \lesssim \|DAD^{-1}\|_{l_2 \to l_2}^2 \|\Psi\|_{H^1}^2 , \quad (5.75)$$

where we have used Theorem 5.16 and the fact that $\|D\mathbf{c}\|_{l_2}^2 = \|\mathbf{c}\|_V^2$. We can now use Theorem 5.17 to estimate the elements of $\tilde{A} := DAD^{-1}$

$$\tilde{a}_{\nu,\mu} = \left(\frac{\varepsilon_\nu}{\varepsilon_\mu} \right)^{1/2} \sum_{\alpha \in \mathcal{I}} t_\alpha \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \leq C \sum_{\alpha \in \mathcal{I}} t_\alpha \varepsilon_\alpha^{1/2} \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle . \quad (5.76)$$

Therefore the operator norm of $\tilde{A}$ can be bounded as follows

$$\|\tilde{A}\|_{l_2 \to l_2} \leq CC_N \left(\sum_{\alpha \in \mathcal{I}} |t_\alpha|^2 \varepsilon_\alpha \right)^{1/2} = CC_N \|t\|_V . \quad (5.77)$$

where C_N is the constant in Lemma 5.1. Hence, for some $G > 0$ we find

$$\|T\Psi\|_{H^1}^2 \leq G\|t\|_V^2 \|\Psi\|_{H^1}^2 \quad (5.78)$$

and therefore

$$\|T\|_{H^1 \to H^1} \leq G\|t\|_V . \quad (5.79)$$

The equivalence of the norm follows from Theorem 5.16 as

$$\|t\|_V \leq G'\|T\Psi_0\|_{H^1} \leq G'\|T\|_{H^1 \to H^1} \quad (5.80)$$

holds for some $G' > 0$. □

We emphasise that due to the uniformity assumptions, the above statement hold uniformly in K which is an essential property for investigation on the boundedness of T for $K \to \infty$. Having established these structures between the cluster amplitude space and the cluster operator space, we can pass on to the first property that is needed for the local version of Zarantonello's theorem.
We point out that the following two theorems are proven in an alternative way to [2].

Theorem 5.19. *The function $f : V \to V'$ is differentiable at $t \in V$. Furthermore, the Fréchet derivative is Lipschitz continuous as well as all higher derivatives. In particular, for any neighbourhood $U_R(0) \subset V$ with $f : U_R(0) \to V'$ there exists a Lipschitz constant $L(R)$ such that*

$$\|f(t_1) - f(t_2)\|_{V'} \leq L(R)\|t_1 - t_2\|_V \tag{5.81}$$

for $\|t_1\|_V$, $\|t_2\|_V \leq R$.

Proof. The derivative of f is given by

$$(f'(t))_{\mu,\nu} = \langle \Psi_\mu, [e^{-T}He^T, X_\nu]\Psi_0 \rangle . \tag{5.82}$$

Using $H : H^1 \to H^{-1}$ we obtain for given $s, u \in V$ that

$$|\langle f'(t)s, u \rangle| = |\langle U\Psi_0, [e^{-T}He^T, S]\Psi_0 \rangle| \leq C\|s\|_V\|u\|_V , \tag{5.83}$$

where U, S are the to u, s corresponding operators. This shows the boundedness of $f'(t) : V \to V'$. Hence, $f : V \to V'$ is differentiable at $t \in V$. By defining the function

$$\varphi : [0, 1] \to V'; x \mapsto f(xt_1 + (1 - x)t_2) \tag{5.84}$$

and applying the mean value theorem we obtain

$$\begin{aligned}
\|f(t_2) - f(t_1)\|_{V'} = \|\varphi(0) - \varphi(1)\|_{V'} &\leq \|\varphi'(c)\|_{V'} \\
&= \|f'(ct_1 + (1 - c)t_2)(t_1 - t_2)\|_{V'} \\
&\leq \|f'(ct_1 + (1 - c)t_2)\|_{L(V,V')}\|(t_1 - t_2)\|_{V'} ,
\end{aligned} \tag{5.85}$$

where t_1, $t_2 \in V_{ext}$ with $\|t_1\|_{V_{ext}}$, $\|t_2\|_{V_{ext}} \leq R$ for some $R > 0$ and $c \in (0, 1)$. Hence, it follows the Lipschitz continuity of f. $\square$

In the following, we show that f is a locally strong monotone function. We prove this property under the following assumptions. We impose:

$$\langle T\Psi_0, (F - \Lambda_0)T\Psi_0 \rangle \geq \eta\|T\Psi_0\|_{H^1}^2 . \tag{5.86}$$

The above boundary is guaranteed by imposing a spectral gap of the Fock operator and a Gårding estimate.
Using the definition $H = F + W$ of the Hamilton operator into the Fock operator F and a fluctuation operator W, we define the operator

$$O : V \to H^{-1}; t \mapsto e^{-T}We^T\Psi_0 . \tag{5.87}$$

We further assume that O is locally Lipschitz continuous with a constant $LC < \eta$ where C is the constant implied by Theorem 5.16 such that $\|t\|_V \leq C\|T\Psi_0\|_{H^1}$ holds. Under these assumptions we can prove the following theorem.

Theorem 5.20. *The CC function f is locally strong monotone.*

Proof. Be B_δ the ball on which O is Lipschitz continuous with a constant $LC < \eta$ and $t_1, t_2 \in B_\delta$. By the definition of the CC function f we note that

$$\langle f(t_1) - f(t_2), t_1 - t_2 \rangle = \langle (T_1 - T_2)\Psi_0, (e^{-T_1} H e^{T_1} - e^{-T_2} H e^{T_2})\Psi_0 \rangle \quad (5.88)$$

holds. We recall that $e^{-T_i} F e^{T_i} = F + [F, T_i]$ according to Lemma 5.13. Inserting the decomposition $H = F + W$ yields

$$
\begin{aligned}
&\langle f(t_1) - f(t_2), t_1 - t_2 \rangle \\
&= \langle (T_1 - T_2)\Psi_0, [F, T_1 - T_2]\Psi_0 \rangle + \langle (T_1 - T_2)\Psi_0, O(t_1) - O(t_2) \rangle \\
&= \langle (T_1 - T_2)\Psi_0, (F - \Lambda_0)(T_1 - T_2)\Psi_0 \rangle + \langle (T_1 - T_2)\Psi_0, O(t_1) - O(t_2) \rangle \\
&\geq \eta \|(T_1 - T_2)\Psi_0\|_{H^1}^2 - \|(T_1 - T_2)\Psi_0\|_{H^1} \|O(t_1) - O(t_2)\|_{H^{-1}} \\
&\geq (\eta - LC)\|(T_1 - T_2)\Psi_0\|_{H^1}^2 \\
&\geq \left(\frac{\eta - LC}{C^2}\right)\|t_1 - t_2\|_{H^1}^2 ,
\end{aligned}
\quad (5.89)
$$

where in addition to the Lipschitz continuity of O we have used that by Theorem 5.16

$$\|t_1 - t_2\|_V \leq C\|(T_1 - T_2)\Psi_0\|_{H^1} \quad (5.90)$$

holds. Hence, f is locally strongly monotone. $\square$

In this subsection we were able to show that under certain assumptions the local version of Zarantonello's theorem is applicable to the projected coupled cluster function. We emphasise that these assumptions are reasonable for the framework of the coupled cluster formalism. We point out that in the case of degenerate states the single-reference coupled cluster method does not yield a good approximation [18]. Here, one needs to use a different approach like the *tailored coupled cluster* method.

5.3 Projected-Coupled-Cluster-Single-Double

In this subsection we analyse the equivalence of linked and unlinked formulation of the truncated projected coupled cluster method. This section is geared to [35] and introduces a structure of prove the equivalence of linked and unlinked coupled cluster equations. We will see in the next chapter on the *tailored coupled cluster* method that this equivalence is in general not given.

We have seen that $\sharp\mathcal{I} = \mathcal{O}(K^N)$ becomes prohibitively large for increasing N. We

therefore want to approximate the projected coupled cluster solution on a subset $\mathcal{I}_h$ that contains much less parameters e.g. $I_2 = \{\mu \in \mathcal{I} | \sharp\mu \leq 2\}$ is the so called coupled cluster single double ansatz (CCSD). We emphasise at this point that much more than single and double amplitudes are rarely calculated in practice.

Remark 5.21. *The previously given definition of the projected coupled cluster function can be used directly for the truncated case. Giving a subset $\mathcal{I}_h \subseteq \mathcal{I}$ and the respective subspace $\mathcal{V}_h \subseteq \mathcal{V}$ we define $t_h := (t_\nu)_{\nu \in \mathcal{I}}$ with $t_\nu = 0$ if $\nu \notin \mathcal{I}_h$. The truncated projected coupled cluster ansatz consists in setting $t_h = (t_\nu)_{\nu \in \mathcal{I}}$ with $t_\nu = 0$ if $\nu \notin \mathcal{I}_h$. We then use the procedure defined in the previous subsection.*

Using the truncated projected coupled cluster ansatz we obtain a set of $L = \sharp\mathcal{I}_h$ equations describing the excitation amplitudes t_μ, $\mu \in \mathcal{I}_h$. In practice one is interested in a way of truncating in a way that keeps the residual and the calculation costs small. The CCSD is the most common usedd coupled cluster method as in the case on dynamic correlation the cluster amplitudes of the triple and higher excitations are negligibly small. However, in the case on static correlation this is no longer the case. We show that for the coupled cluster method the linked and unlinked equations are equivalent under truncating the excitation rank at a certain order, i.e. CCSD, CCSDT, etc..

Theorem 5.22. *$K, N \in \mathbb{N}$ with $K > N$ fixed, $\{\varphi_1, ..., \varphi_K\}$ a set of orthonormal spin orbitals and Ψ_0 a reference Slater determinant. For any $\mathcal{I}_h \subseteq \mathcal{I}$ with $\sharp\mathcal{I}_h \leq N$*

$$\begin{cases} \langle \Psi_\mu, H e^{T_h} \Psi_0 \rangle = E_h^{(CC)} \langle \Psi_\mu, e^{T_h} \Psi_0 \rangle & , \mu \in \mathcal{I}_h \ , \\ \langle \Psi_0, H e^{T_h} \Psi_0 \rangle = E_h^{(CC)} \end{cases} \tag{5.91}$$

is equivalent to

$$\begin{cases} \langle \Psi_\mu, e^{-T_h} H e^{T_h} \Psi_0 \rangle = 0 & , \mu \in \mathcal{I}_h \ , \\ \langle \Psi_0, e^{-T_h} H e^{T_h} \Psi_0 \rangle = E_h^{(CC)} \ . \end{cases} \tag{5.92}$$

Proof. In contrast to the proof of Theorem 5.7 this is not trivial to show. We consider a truncation of the ansatz space such that we have $\sharp\mathcal{I}_h$ excitation amplitudes. Due to the orthogonality of the state function we can deduce

$$\mathcal{R}(\Psi_0) \circ \exp(-T_h) = \mathcal{R}(\Psi_0) \ . \tag{5.93}$$

Hence, analogously to the proof of Theorem 5.7 we obtain

$$\langle \Psi_0, H e^{T_h} \Psi_0 \rangle = \langle \Psi_0, e^{-T_h} H e^{T_h} \Psi_0 \rangle = E_0^{(CC)} \ . \tag{5.94}$$

For the other equations we define the operator

$$\mathbf{T} = (T)_{\mu, \nu \in \mathcal{I}_h} \in \mathbb{R}^{\sharp\mathcal{I}_h \times \sharp\mathcal{I}_h} \ , \tag{5.95}$$

with

$$T_{\mu,\nu} = \langle \Psi_\mu, e^{T_h} \Psi_\nu \rangle = \langle \Psi_\mu, \Psi_\nu \rangle + \langle \Psi_\mu, T\Psi_\nu \rangle + \frac{1}{2} \langle \Psi_\mu, T^2 \Psi_\nu \rangle + \dots \ . \tag{5.96}$$

As T_h only increases the excitation rank this matrix has an upper triangular shape. Due to the orthonormality of the states the diagonal consists of ones. This structure is depicted in the following block Fig. 5.1 representation.

	0	S	D	$\cdots$	M
0	1	0	0	$\cdots$	0
S		1	0	$\cdots$	0
D			1	$\ddots$	0
$\vdots$				$\ddots$	0
M					1

Figure 5.1: Block representation of the operator T.

Due to its triangular shape, the matrix $\mathbf{T}$ is not singular. We now assume that the linked equations hold true. As the matrix $\mathbf{T}$ is not singular the linked equations are equivalent to

$$
\begin{aligned}
A_\mu &:= \sum_{\nu \in \mathcal{I}_h} T_{\mu,\nu} \left\langle \Psi_\nu, e^{-T_h} H e^{T_h} \Psi_0 \right\rangle = \sum_{\nu \in \mathcal{I}_h} \left\langle \Psi_\mu, e^{T_h} \Psi_\nu \right\rangle \left\langle \Psi_\nu, e^{-T_h} H e^{T_h} \Psi_0 \right\rangle \\
&\underset{(1)}{=} \sum_{\nu \in \mathcal{I}_h} \mathcal{R}(\Psi_\mu)(e^{T_h} \Psi_\nu) \mathcal{R}(\Psi_\nu)(e^{-T_h} H e^{T_h} \Psi_0) \\
&\underset{(2)}{=} \left(\mathcal{R}(\Psi_\mu) \circ e^{T_h} \right) \left(\sum_{\nu \in \mathcal{I}_h} \Psi_\nu \mathcal{R}(\Psi_\nu)(e^{-T_h} H e^{T_h} \Psi_0) \right) \\
&= 0
\end{aligned}
\tag{5.97}
$$

for all $\mu \in \mathcal{I}_h$. Due to the orthogonality of the state functions the identity on $\mathcal{V}_h$ can be written as

$$I = \sum_{\nu \in \mathcal{I}_h} \Psi_\nu \mathcal{R}(\Psi_\nu) + \Psi_0 \mathcal{R}(\Psi_0) \tag{5.98}$$

which is equivalent to

$$\sum_{\nu \in \mathcal{I}_h} \Psi_\nu \mathcal{R}(\Psi_\nu) = I - \Psi_0 \mathcal{R}(\Psi_0) \ . \tag{5.99}$$

This yields

$$0 = A_\mu = \left(\mathcal{R}(\Psi_\mu) \circ e^{T_h}\right)(e^{-T_h} H e^{T_h} \Psi_0) \tag{5.100a}$$
$$- \left(\mathcal{R}(\Psi_\mu) \circ e^{T_h}\right)(\Psi_0 \mathcal{R}(\Psi_0)(e^{-T_h} H e^{T_h} \Psi_0)) . \tag{5.100b}$$

We start by analysing Eq. (5.100a). We find

$$\left(\mathcal{R}(\Psi_\mu) \circ e^{T_h}\right)(e^{-T_h} H e^{T_h} \Psi_0) = \langle \Psi_\mu, e^{T_h} e^{-T_h} H e^{T_h} \Psi_0 \rangle = \langle \Psi_\mu, H e^{T_h} \Psi_0 \rangle . \tag{5.101}$$

For Eq. (5.100b) we obtain

$$\left(\mathcal{R}(\Psi_\mu) \circ e^{T_h}\right)(\Psi_0 \mathcal{R}(\Psi_0)(e^{-T_h} H e^{T_h} \Psi_0)) = \mathcal{R}(\Psi_0)(e^{-T_h} H e^{T_h} \Psi_0) \left(\mathcal{R}(\Psi_\mu) \circ e^{T_h}\right)(\Psi_0)$$
$$= \underbrace{\langle \Psi_0, e^{-T_h} H e^{T_h} \Psi_0 \rangle}_{=E} \langle \Psi_\mu, e^{T_h} \Psi_0 \rangle$$
$$= E_h^{(CC)} \langle \Psi_\mu, e^{T_h} \Psi_0 \rangle \tag{5.102}$$

In conclusion we obtain

$$\langle \Psi_\mu, H e^{T_h} \Psi_0 \rangle = E_h^{(CC)} \langle \Psi_\mu, e^{T_h} \Psi_0 \rangle \tag{5.103}$$

which was the claim. $\qquad\square$

We will see that in the case of the *tailored coupled cluster* method this equivalence is no longer given. We also want to point out that this equivalence only holds for the truncations of the ansatz space up to a certain excitation level. For general truncations of the ansatz space this equivalence is not given, see [35].

6 Tailored Coupled Cluster Method

In the previous two chapters we have discussed the full-CI method and the projected coupled cluster method. The full-CI method was numerically very costly as the ansatz space scales with $\mathcal{O}(K^N)$ but had all the benefits of a discrete Galerkin scheme independent of the electron correlation [35]. The projected coupled cluster method yields very accurate solutions for dynamical electron correlation [35, 18]. The disadvantage of the single-reference coupled cluster ansatz is that for static electron correlation the high accuracy is no longer guaranteed.

There are several way to avoid the high costs of the full-CI method and still get fairly accurate results, see [18]. One way of fixing the single-reference coupled cluster ansatz to deal with static correlation is the externally corrected ansatz [18]. Here, the wave function is split into two parts: a fixed part imported from a full-CI calculation and the dynamic exponential coupled cluster part, which is adjusted in the presents of the fixed full-CI part.

Hereby, we focus on the so called *tailored coupled cluster (TCC)* method [19] especially a method called *density matrix renormalisation group tailored coupled cluster (DMRG-TCC)* method [1], which uses the DMRG to approximate the full-CI solution used in the TCC method. As the scaling of full-CI like calculations suffers from the curse of dimensionality it is notable that the following method is only suited for systems where the static correlation can be calculated with a *small* full-CI calculation.

The idea is to approximate the correlation with a dynamical and a non-dynamical part

$$\Psi_0^{TCC} = exp(T^{ext})exp(T^{CAS})\Psi_0 \ , \tag{6.1}$$

where $exp(T^{CAS})$ is extracted from the CI coefficients of the CAS-CI wave function. It remains to calculate the excitation amplitudes for the operator $exp(T^{ext})$ describing the dynamic electron correlation.

Subsequently, we formulate the *tailored coupled cluster* method a in mathematical framework and present a first analysis of it. We emphasise that unlike in the coupled cluster framework the assumption of the existence of a HOMO-LUMO gap is no longer reasonable. This is due to the fact that we consider strongly correlated systems where numerous states can be almost degenerate.

6.1 Analysis of the Tailored Coupled Cluster Method

In this subsection we follow the same structure as in the subsection on the analysis of the projected coupled cluster method. We start by giving a mathematical definition of the tailored coupled cluster method. Thereafter, we pass on to establishing the needed properties to apply the local version of Zarantonello's theorem to the tailored coupled cluster method.

We start by introducing a *spin orbital splitting*. The given set of spin orbitals is split into two parts: a *complete active space part* and a *external space part*.

Definition 6.1. *Be $\{\varphi_1, ..., \varphi_K\}$ a set of orthonormal spin orbitals with $K > N$ and Ψ_0 the considered reference Slater determinant. We define*

$$
\mathscr{B}_{CAS} = \{\underbrace{\varphi_1, ..., \varphi_N}_{occupied}, \underbrace{\varphi_{N+1}, ..., \varphi_d}_{unoccupied}\} \ ,
$$
$$
\mathscr{B}_{ext} = \{\underbrace{\varphi_{d+1}, ..., \varphi_K}_{external}\} \ ,
$$
(6.2)

*the basis sets of the **complete active space part** $\mathscr{B}_{CAS}$ and of the **external space part** $\mathscr{B}_{ext}$.*

Using the complete active space part $\mathscr{B}_{CAS}$ we define the corresponding full configuration interaction space $\mathcal{V}_{CAS}$.

Analogously we split the set of multi-indices $\mathcal{I}$ describing the set of possible excitations. We define

$$
\mathcal{I}_{CAS} := \{\mu \in \mathcal{I} | X_\mu \Psi_0 \in \mathcal{V}_{CAS}\}
$$
(6.3)

and

$$
\mathcal{I}_{ext} := \{\mu \in \mathcal{I} | X_\mu \Psi_0 \notin \mathcal{V}_{CAS}\} \ .
$$
(6.4)

Remark 6.2.

i) *The choice of this basis splitting is not arbitrary. For the correctness of the tailored coupled cluster scheme it is important that $\mathscr{B}_{CAS}$ covers the strongly correlated spin orbitals and that $\mathscr{B}_{ext}$ consists only of spin orbitals with dynamic electron correlation. Further it is notable that $\mathcal{I}_{ext}$ does not only contain excitations into states purely excited in $\mathscr{B}_{ext}$ but also into **mixed** states. In these mixed states, the spin orbitals of Ψ_0 are not exclusively exchanged by spin orbitals from $\mathscr{B}_{ext}$ but also $\mathscr{B}_{CAS}$.*

ii) *One disadvantage of the TCC method can be seen already: It needs further expertise on how to split the amplitudes. Therefore it can not be implemented as a black box to perform quantum chemical calculations.*

Subsequently we assume that a suitable basis splitting is possible and already performed. As mentioned above the *tailored coupled cluster* method can be understood as a coupled cluster method tailored by a full-CI solution Ψ_{CAS}. This full-CI solution is calculated in the full-CI space $\mathcal{V}_{CAS}$ defined by the spin orbitals $\mathscr{B}_{CAS}$ from the previously defined partition of the spin orbital set. As we have seen in the section on the full configuration interaction method the full-CI solution Ψ_{CAS} can be formulated with an excitation operator acting on a reference state Ψ_0:

$$\Psi_{CAS} = (I + \tilde{T}^{CAS})\Psi_0 . \tag{6.5}$$

Due to the one-to-one relation of such excitation operators and cluster operators established in Theorem 5.4 we find the corresponding cluster operator T^{CAS} such that

$$\Psi_{CAS} = e^{T^{CAS}}\Psi_0 . \tag{6.6}$$

Hence, having a CAS-CI wave function it only remains to calculate the cluster amplitudes of the TCC-Cluster operator that describes excitations apart from those into the complete active space part. The cluster operator defined by these remaining amplitudes is denoted T^{ext}. In conclusion, we formulate the linked TCC-equations as

$$
\begin{cases}
E_0^{(TCC)} = \left\langle \Psi_0, e^{-T^{CAS}}e^{-T^{ext}}He^{T^{CAS}}e^{T^{ext}}\Psi_0 \right\rangle , \\
\quad\quad 0 = \left\langle \Psi_\mu, e^{-T^{CAS}}e^{-T^{ext}}He^{T^{CAS}}e^{T^{ext}}\Psi_0 \right\rangle, \quad \mu \notin \mathcal{I}_{CAS} .
\end{cases}
\tag{6.7}
$$

The tailored coupled cluster method can therefore be understood as a split amplitude ansatz. Having introduced this connection to the single-reference coupled cluster method we pass on to defining the *tailored coupled cluster* method in the same way as we defined the projected coupled cluster method. We introduce the *tailored coupled cluster function*.

Definition 6.3. *Be $K, N \in \mathbb{N}$ with $K > N$ fixed $\mathscr{B} = \{\varphi_1, ..., \varphi_K\}$ a set of orthonormal spin orbitals and Ψ_0 a reference state for an N electron problem. Further, be $\mathscr{B}_{CAS}$ and $\mathscr{B}_{ext}$ a given partition of $\mathscr{B}$ and Ψ_{CAS} the full-CI solution on the complete active space $\mathcal{V}_{CAS}$. For $t = (t_\nu)_{\nu \in \mathcal{I}_{ext}} \in \mathbb{R}^{\sharp \mathcal{I}_{ext}}$ we define*

$$f : \mathbb{R}^{\sharp \mathcal{I}_{ext}} \to \left(\mathbb{R}^{\sharp \mathcal{I}_{ext}}\right)'; \; t \mapsto (f_\mu(t))_{\mu \in \mathcal{I}_{ext}} \tag{6.8}$$

where

$$
\begin{aligned}
f_\mu(t) &= \langle \Psi_\mu, e^{-T^{CAS}}e^{-T}He^{T}e^{T^{CAS}}\Psi_0 \rangle \\
&= \langle \Psi_\mu, e^{-T^{CAS}} \exp(-\sum_{\nu \in \mathcal{I}_{ext}} t_\nu X_\nu) H \exp(\sum_{\nu \in \mathcal{I}_{ext}} t_\nu X_\nu)e^{T^{CAS}}\Psi_0 \rangle
\end{aligned}
\tag{6.9}
$$

as the **Tailored Coupled Cluster function**. *We call* $V_{ext} := \mathbb{R}^{\sharp \mathcal{I}_{ext}}$ **the space of external cluster amplitudes**. *We further denote*

$$\mathcal{V}_{ext} = \{T \, \Psi_{CAS} \mid t \in V_{ext}\} \tag{6.10}$$

the **external space**.

In analogy to the previous chapter we define the norm on the external amplitude space.

Definition 6.4. *The map*

$$\| \cdot \|_{V_{ext}} : V_{ext} \to \mathbb{R}; t \mapsto \|t\|_{V_{ext}} = \sqrt{\sum_{\mu \in \mathcal{I}_{ext}} \varepsilon_\mu |t_\mu|^2} \tag{6.11}$$

is called the **external cluster amplitude norm**.

Remark 6.5.

 i) *Due to simplicity and the fact that there exists a one to one relation between cluster amplitudes and cluster operators, we use again capital letters with a respective exponential suffix for the state space (ext or CAS) for the cluster operators corresponding to the cluster amplitudes denoted by small letters.*

 ii) *We see that the linked coupled cluster equations (6.7) can be formulated as*

$$f(t) = 0 \tag{6.12}$$

 or

$$\langle v, f(t) \rangle = 0 \quad , \forall \; v \in V_{ext} \; . \tag{6.13}$$

Subsequently, we consider the tailored coupled cluster method as a Galerkin method applied to the non-linear equation $f((t_\nu)_{\nu \in \mathcal{I}_{ext}}) = 0$. We prove that the local version of Zarantonello's theorem is applicable. Analogously to the analysis presented in the previous section we establish a relationship between the norm of the amplitude vector $(t_\nu)_{\nu \in \mathcal{I}_{ext}}$ and the H^1-norm of the therewith defined state function $\Psi = T^{ext}((t_\nu)_{\nu \in \mathcal{I}_{ext}})\Psi_{CAS} = T^{ext}\Psi_{CAS}$.

As we have mentioned before, the assumption of the existence of a HOMO-LUMO gap is no longer reasonable. In the context of the tailored coupled cluster method it seems straightforward to think about a gap between the complete active space and an external space, i.e. λ_d and λ_{d+1} are gaped. Even though this gap appears to be reasonable we introduce the larger CAS-EXT gap between λ_N and λ_{d+1}. As

this gap is larger it has the advantage of yielding better constants in the following estimates. Additionally, this gap is steerable by the choice of the complete active space, i.e. choosing a large complete active space yields a large λ_{d+1} and therewith a large CAS-EXT gap. In analogy to the previous chapter, we denote the CAS-EXT gap by $\varepsilon_0 = \lambda_{d+1} - \lambda_N$. We generalise the theorems, presented in the previous chapter, to holds true for a CAS-EXT gap. From now on we assume the existence of such a CAS-EXT gap.

Theorem 6.6. *For $t \in V_{ext}$ and $T^{ext} := \sum_{\mu \in \mathcal{I}} t_\mu X_\mu$ there holds*

$$\|t\|_{V_{ext}} \sim \|T^{ext}\Psi_{CAS}\|_{H^1} \ . \tag{6.14}$$

Proof. Be $T := T^{ext} = \sum_{\mu \in \mathcal{I}_{ext}} t_\mu X_\mu$. We know that by Lemma 5.13 $e^T F e^T = F + [F, T]$ holds. With Ψ_0 being the eigenfunction of the Fock operator $F : \mathcal{V}_K \to \mathcal{V}'_K$ to the lowest eigenvalue Λ_0. We find

$$\langle \phi, e^T F e^T \Psi_0 \rangle = \langle \phi, \Lambda_0 \Psi_0 + \sum_{\mu \in \mathcal{I}_{ext}} \varepsilon_\mu t_\mu \Psi_\mu \rangle \ . \tag{6.15}$$

Choosing $\phi = T\Psi_0$ yields

$$\|t\|_{V_{ext}}^2 = \|t\|_V^2 = \sum_{\mu \in \mathcal{I}_{ext}} \varepsilon_\mu |t_\mu|^2 = \langle T\Psi_0, \Lambda_0 \Psi_0 + \sum_{\mu \in \mathcal{I}_{ext}} \varepsilon_\mu t_\mu \Psi_\mu \rangle \ . \tag{6.16}$$

As $\mu \in \mathcal{I}_{ext}$ the $\varepsilon_\mu = \sum_{i=1}^k \lambda_{a_i} - \lambda_{l_i} \geq \varepsilon_0 = \lambda_{d+1} - \lambda_N$ are bounded by the CAS-EXT gap. Further it holds $\langle \phi, (F - \Lambda_0)\Psi_0 \rangle = 0$ for all $\phi \in \mathcal{V}_K$. We can conclude that a lower estimate of the spectrum of the matrix $(\langle \Psi_\mu, (F - \Lambda_0)\Psi_\nu \rangle)_{\mu, \nu \in \mathcal{I}_{ext}}$ is provided by ε_0. This implies $\|\phi\|_{H^1}^2 \sim \langle \phi, (F - \Lambda_0)\phi \rangle$ for all $\phi \perp \text{CAS}, \ \phi \in \mathcal{V}_K$. We estimate for $\phi := T\Psi_0$

$$\|\phi\|_{H^1}^2 = \|T\Psi_0\|_{H^1}^2 \sim \langle T\Psi_0, (F - \Lambda_0)T\Psi_0 \rangle = \sum_{\mu \in \mathcal{I}_{ext}} \varepsilon_\mu |t_\mu|^2 = \|t\|_V^2 = \|t\|_{V_{ext}}^2 \tag{6.17}$$

From this norm equivalence we can deduce further that

$$\begin{aligned}
\|t\|_{V_{ext}} &\leq C\|T^{ext}\Psi_0\|_{H^1} = C\|e^{T^{CAS}} e^{-T^{CAS}} T^{ext}\Psi_0\|_{H^1} \\
&\leq C\|e^{-T^{CAS}}\|_{H^1 \to H^{-1}} \|T^{ext}\Psi_{CAS}\|_{H^1}
\end{aligned} \tag{6.18}$$

and

$$\|t\|_{V_{ext}} \geq C\|T^{ext}\Psi_0\|_{H^1} = \underbrace{\frac{C}{\|e^{T^{CAS}}\|_{H^1 \to H^{-1}}}}_{\tilde{C}} \|e^{T^{CAS}}\|_{H^1 \to H^{-1}} \|T^{ext}\Psi_0\|_{H^1} \tag{6.19}$$

$$\geq \tilde{C}\|T^{ext}\Psi_{CAS}\|_{H^1} \ .$$

This yields that $\|t\|_{ext} \sim \|T^{ext}\Psi_{CAS}\|_{H^1}$. $\qquad\square$

This theorem states that the norm of a state function generated by the cluster operator $T^{ext}T^{CAS}$ for a fixed T^{CAS} can be expressed by using the norm of the cluster amplitudes $(t_\mu)_{\mu \in \mathcal{I}_{ext}}$. This is indeed the measure we are interested in as the CAS-CI solution Ψ_{CAS} is calculated by a DMRG scheme and is fixed throughout the coupled cluster calculations. Hence, a measure of the state functions H^1-norm estimated by the respective external cluster amplitudes is of interest.

In the same way, we want to measure the operator norm of T^{ext} by using only the external cluster amplitudes. Analogously to the previous section, we make use of the following lemma. We emphasise that we can not generalise the Lemma 5.17 such that it holds for a CAS-EXT gap. However, we find enough structure to show the desired norm equivalence.

Lemma 6.7. *Be $\nu \in \mathcal{I}_{ext}$ and $\alpha, \mu \in \mathcal{I}$ with $\sharp\alpha,\ \sharp\mu \le \sharp\nu$ and $\alpha = \nu \ominus \mu$ such that $\langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \ne 0$, then there exists a constant C such that*

i)

$$\frac{\varepsilon_\nu}{\varepsilon_\mu} \le C \varepsilon_\alpha \qquad , \text{ if } \alpha,\ \mu \in \mathcal{I}_{ext} , \tag{6.20}$$

ii)

$$\varepsilon_\nu \le C \varepsilon_\alpha \qquad , \text{ if } \alpha \in \mathcal{I}_{ext} \text{ and } \mu \in \mathcal{I}_{CAS} . \tag{6.21}$$

Proof. We recall $\varepsilon_0 = \lambda_{d+1} - \lambda_N$ is the CAS-EXT gap. Then for all $\nu \in \mathcal{I}_{ext}$ we find $0 < \varepsilon_0 \le \varepsilon_\nu$ and equivalently $\varepsilon_0^{-1} \ge \varepsilon_\nu^{-1}$. Further for all $\nu \in \mathcal{I}_{ext}$

$$0 \le \overline{\lambda}_\nu := max\{\lambda_{a_i} | i = 1, ..., \sharp\nu\} - \delta , \tag{6.22}$$

where $\delta := (\lambda_{d+1} + \lambda_N)/2$. We conclude that $\varepsilon_\nu \le N(\overline{\lambda}_\nu - (\lambda_1 - \delta))$ and $\overline{\lambda}_\nu > \varepsilon_0/2$ which is equivalent to $(2\overline{\lambda}_\nu)^{-1} < \varepsilon_0^{-1}$. This implies $|\lambda_1 - \delta| = 2|\lambda_1 - \delta|\overline{\lambda}_\nu/(2\overline{\lambda}_\nu) \le 2|\lambda_1 - \delta|\overline{\lambda}_\nu/\varepsilon_0$. Hence for all $\nu \in \mathcal{I}_{ext}$ there exists a $C > 0$ with

$$C^{-1}\varepsilon_\nu \le \overline{\lambda}_\nu \le \varepsilon_\nu . \tag{6.23}$$

By assumption it holds $\Psi_\nu = X_\alpha \Psi_\mu$. We consider three cases:

i) Be $\alpha,\ \mu \in \mathcal{I}_{ext}$ and $\overline{\lambda}_\alpha \ge \overline{\lambda}_\mu$. Then $\overline{\lambda}_\alpha = \overline{\lambda}_\nu$ and we can estimate

$$\frac{\varepsilon_\nu}{\varepsilon_\mu} \le \frac{C\overline{\lambda}_\nu}{\varepsilon_0} = \frac{C}{\varepsilon_0}\overline{\lambda}_\alpha \le \frac{C}{\varepsilon_0}\varepsilon_\alpha . \tag{6.24}$$

ii) Be $\alpha,\ \mu \in \mathcal{I}_{ext}$ and $\overline{\lambda}_\alpha \le \overline{\lambda}_\mu$. Then $\overline{\lambda}_\mu = \overline{\lambda}_\nu$ and we can estimate

$$\frac{\varepsilon_\nu}{\varepsilon_\mu} \le \frac{C\overline{\lambda}_\nu}{\overline{\lambda}_\mu} = C = \frac{2\overline{\lambda}_\alpha}{2\overline{\lambda}_\alpha}C \le \frac{2C}{\varepsilon_0}\varepsilon_\alpha . \tag{6.25}$$

iii) Be $\alpha \in \mathcal{I}_{ext}$ and $\mu \in \mathcal{I}_{CAS}$. Then $\overline{\lambda}_\alpha = \overline{\lambda}_\nu$ and we can estimate

$$\varepsilon_\nu \leq C\overline{\lambda}_\nu = C\overline{\lambda}_\alpha \leq C\varepsilon_\alpha \ . \tag{6.26}$$

$\square$

Using the previous two theorems we can prove the following theorem describing the equivalence of the operator norm of T^{ext} and the corresponding external cluster amplitudes $(t_\mu)_{\mu \in \mathcal{I}_{ext}}$.

Theorem 6.8. *Be $t \in V_{ext}$. The operator $T = \sum_{\nu \in \mathcal{I}_{ext}} t_\nu X_\nu$ satisfies under the assumption of a CAS-EXT gap the estimate*

$$\|T\Psi\|_{H^1} \leq C\|t\|_{V_{ext}}\|\Psi\|_{H^1} \tag{6.27}$$

for all $\Psi \in \mathcal{V}_K$. Moreover, the operator norm of the operator T is equivalent to $\|t\|_{V_{ext}}$, we write

$$\|T\|_{H^1 \to H^1} \sim \|t\|_{V_{ext}} \ . \tag{6.28}$$

Proof. Let $\Psi = \sum_{\mu \in \mathcal{I}} c_\mu \Psi_\mu \in \mathcal{V}_K$, $T = \sum_{\alpha \in \mathcal{I}_{ext}} t_\alpha X_\alpha$ and $c = (c_\mu)_{\mu \in \mathcal{I}}$ where we assume w.l.o.g. that $(c_\mu)_{\mu \in \mathcal{I}} = ((c_\mu)_{\mu \in \mathcal{I}_{ext}}, (c_\mu)_{\mu \in \mathcal{I}_{CAS}})$. From Theorem 6.6 we can deduce that

$$\|T\Psi\|_{H^1}^2 \sim \|(\langle \Psi_\nu, T\Psi \rangle)_{\nu \in \mathcal{I}_{ext}}\|_V^2$$
$$= \sum_{\nu \in \mathcal{I}_{ext}} \left(\varepsilon_\nu^{1/2} | \sum_{\alpha \in \mathcal{I}_{ext}} \sum_{\mu \in \mathcal{I}} t_\alpha c_\mu \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle | \right)^2 \ . \tag{6.29}$$

Defining the following three matrices

$$A := (\langle \Psi_\nu, T\Psi_\mu \rangle)_{\nu \in \mathcal{I}_{ext}, \mu \in \mathcal{I}} \quad D := diag(\varepsilon_\nu^{1/2})_{\nu \in \mathcal{I}_{ext}} \quad \tilde{D} := \left(\begin{array}{c|c} D & 0 \\ \hline 0 & I \end{array} \right) \tag{6.30}$$

we can rewrite Eq. (6.29)

$$\|t\|_V^2 \sim \|DA\tilde{D}^{-1}\tilde{D}c\|_{l^2}^2 \ . \tag{6.31}$$

We recall that we are assuming that $\mu \in \mathcal{I}$ is ordered such that $\mu = (\mu_{\mathcal{I}_{ext}}, \mu_{\mathcal{I}_{CAS}})$. We estimate the spectral norm of $\tilde{A} := DA\tilde{D}^{-1}$. We consider the following two cases:

i) Be $\mu \in \mathcal{I}_{ext}$. Then

$$\tilde{a}_{\nu,\mu} = \left(\frac{\varepsilon_\nu}{\varepsilon_\mu} \right)^{1/2} \sum_{\alpha \in \mathcal{I}_{ext}} t_\alpha \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \lesssim \sum_{\alpha \in \mathcal{I}_{ext}} t_\alpha \varepsilon_\alpha^{1/2} \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \ . \tag{6.32}$$

ii) Be $\mu \in \mathcal{I}_{CAS}$. Then

$$\tilde{a}_{\nu,\mu} = \varepsilon_\nu^{1/2} \sum_{\alpha \in \mathcal{I}_{ext}} t_\alpha \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \lesssim \sum_{\alpha \in \mathcal{I}_{ext}} t_\alpha \varepsilon_\alpha^{1/2} \langle \Psi_\nu, X_\alpha \Psi_\mu \rangle \ . \qquad (6.33)$$

Here we have used Lemma 6.7. Hence,

$$\|\tilde{A}\|_{l^2 \to l^2} \leq C \left(\sum_{\alpha \in \mathcal{I}_{ext}} |t_\alpha|^2 \varepsilon_\alpha \right)^{1/2} = C\|t\|_V = C\|t\|_{V_{ext}} \ . \qquad (6.34)$$

Therefore $C\|t\|_{V_{ext}}^2$ is an upper bound of the operator norm of T. The norm equivalence follows with

$$\|t\|_{V_{ext}} \sim \|T\Psi\|_{H^1} \sim \|T\|_{H^1 \to H^1} \ . \qquad (6.35)$$
$$\square$$

Remark 6.9. *In analogy to the proof of Theorem 5.18, the constant C, introduced in the proof above, contains the number of all possible excitations into the respective spin orbitals. This number is quantified in Lemma 5.1 and grows exponentially with considered number of particles. It is in particular not sharp. We emphasise that in the case of the later discussed DMRG-TCCSD the constants describing the norm equivalence are much smaller than those estimated here.*

The theorem above states that the H^1-norm of a state function $\Psi \in \mathcal{V}_{ext}$ created by the cluster operator T^{ext} acting on Ψ_{CAS} can be expressed by the respective norm on the amplitude state V_{ext}. This theorem is a direct transition of the respective result for the projected method. However, we emphasise that unlike in the coupled cluster method we only vary a subset of cluster amplitudes, namely those in V_{ext}. Therefore, in the context of the tailored coupled cluster method, where a full-CI solution Ψ_{CAS} in $\mathcal{V}_{CAS}$ is given, the H^1-norm equivalence to states of the form $T^{ext}\Psi_{CAS}$ and not $T^{ext}\Psi_0$ is of interest. We further emphasise that up to this point we assumed a fixed set of spin orbitals $\{\varphi_1, ..., \varphi_K\}$. Hence, it is important to notice that the constants involved in the norm equivalences depend very likely on K and the respective spaces defined by the fixed number of spin orbitals. Despite its importance, we leave these uniformity assumptions for future analysis.

We move on to proving the Lipschitz continuity of the tailored coupled cluster function. We recall that this is the first property needed to apply the local version of Zarantonello's theorem.

Theorem 6.10. *The function $f : V_{ext} \to V'_{ext}$ is differentiable at $t \in V_{ext}$. Furthermore, the Fréchet derivative is Lipschitz continuous as well as all higher derivatives. In particular, for any neighbourhood $U_R(0) \subset V_{ext}$ with $f : U_R(0) \to V'_{ext}$ there exists a Lipschitz constant $L(R)$ such that*

$$\|f(t) - f(t')\|_{V'_{ext}} \leq L(R)\|t_1 - t_2\|_{V_{ext}} \tag{6.36}$$

for $\|t_1\|_{V_{ext}}, \ \|t_2\|_{V_{ext}} \leq R$.

Proof. We find for the derivative

$$(f'(t))_{\mu,\nu} = \langle \phi_\mu, e^{-T}[e^{-T_{\text{CAS}}}He^{T_{\text{CAS}}}, X_\nu]e^T\phi_0 \rangle \ . \tag{6.37}$$

Using $H : H^1 \to H^{-1}$ we obtain for given $s, u \in V_{\text{ext}}$ that

$$
\begin{aligned}
|\langle f'(t)s, u \rangle| &= |\langle U\phi_0, e^{-T}[e^{-T_{\text{CAS}}}He^{T_{\text{CAS}}}, S]e^T\phi_0 \rangle| \\
&\leq C\|s\|_{V_{\text{ext}}}\|u\|_{V_{\text{ext}}} \ ,
\end{aligned}
\tag{6.38}
$$

where U, S are the to u, s corresponding operators. This shows the boundedness of $f'(t) : V_{\text{ext}} \to V'_{\text{ext}}$. Hence, $f : V_{ext} \to V'_{ext}$ is differentiable at $t \in V_{ext}$. By defining the function

$$\varphi : [0,1] \to V'_{ext}; x \mapsto f(xt_1 + (1-x)t_2) \tag{6.39}$$

and applying the mean value theorem we obtain

$$
\begin{aligned}
\|f(t_2) - f(t_1)\|_{V'_{ext}} &= \|\varphi(0) - \varphi(1)\|_{V'_{ext}} \leq \|\varphi'(c)\|_{V'_{ext}} \\
&= \|f'(ct_1 + (1-c)t_2)(t_1 - t_2)\|_{V'_{ext}} \\
&\leq \|f'(ct_1 + (1-c)t_2)\|_{L(V_{ext}, V'_{ext})}\|(t_1 - t_2)\|_{V'_{ext}} \ ,
\end{aligned}
\tag{6.40}
$$

where t_1, $t_2 \in V_{ext}$ with $\|t_1\|_{V_{ext}}, \ \|t_2\|_{V_{ext}} \leq R$ for some $R > 0$ and $c \in (0,1)$. Hence, it follows the Lipschitz continuity of f. $\square$

Analogously to the previous section we impose:

$$\langle T\phi_0, (\hat{F} - \Lambda_0)T\phi_0 \rangle \geq \eta\|T\phi_0\|^2_{H^1}. \tag{6.41}$$

Up to this point we did not have to make any assumptions on Ψ_{CAS}. To prove that f is locally strong monotone we assume that the operator defined by

$$O : V_{ext} \to H^1; t \mapsto e^{-T}e^{-T^{CAS}}We^{T^{CAS}}e^T\Psi_0 \tag{6.42}$$

is locally monotone with a Lipschitz constant $L > 0$ fulfilling

$$L < \frac{\eta}{C\|e^{T^{CAS}}\|^2_{H^1 \to H^1}\|e^{-T^{CAS}}\|_{H^1 \to H^1}} \ , \tag{6.43}$$

where C is the constant from Theorem 6.6 such that $\|t\|_{V_{ext}} \leq C\|T\Psi_{CAS}\|_{H^1}$ holds. Here, we have used the decomposition $H = F + W$ of the Hamilton operator into the Fock operator F and a fluctuation operator W. The validity of above estimate is dependant on the CAS-CI solution Ψ_{CAS} and is left for future analysis.

Under these assumptions we are now able to prove the local strong monotonicity of the tailored coupled cluster function f.

Theorem 6.11. *The tailored coupled cluster function f is locally strong monotone.*

Proof. Be $t_1, t_2 \in V_{ext}$. By the definition of the tailored coupled cluster function f and the above introduced splitting of the Hamilton operator $H = F + W$ we find

$$
\begin{aligned}
\langle f(t_1) - f(t_2), t_1 - t_2 \rangle &= \langle (T_1 - T_2)\Psi_0, e^{-T_{\text{CAS}}}(H_{t_1} - H_{t_2})e^{T_{\text{CAS}}}\Psi_0 \rangle \\
&= \langle (T_1 - T_2)\Psi_0, e^{-T_{\text{CAS}}}(\exp(-T_1)F\exp(T_1) - \exp(-T_2)F\exp(T_2))e^{T_{\text{CAS}}}\Psi_0 \rangle \\
&\quad + \langle (T_1 - T_2)\Psi_0, O(t_1) - O(t_2) \rangle \\
&= \langle (T_1 - T_2)\Psi_0, e^{-T_{\text{CAS}}}[F, T_1 - T_2]e^{T_{\text{CAS}}}\Psi_0 \rangle \\
&\quad + \langle (T_1 - T_2)\Psi_0, O(t_1) - O(t_2) \rangle ,
\end{aligned}
$$
(6.44)

where $H_{t_i} := \exp(-T_i)H\exp(T_i)$.

Using Lemma 5.13 we find

$$
[F, e^{T_{\text{CAS}}}] = \sum_{n=1}^{N} \frac{1}{n!} \sum_{\mu \in \mathcal{J}_{\text{CAS}}} (t_{\text{CAS}}^{(n)})_\mu X_\mu =: S .
$$
(6.45)

As an excitation operator the operator S commutes with $e^{\pm T_{\text{CAS}}}$ and $\Delta T := T_1 - T_2$. Therefore,

$$
\begin{aligned}
e^{-T_{\text{CAS}}}[F, \Delta T]e^{T_{\text{CAS}}} &= e^{-T_{\text{CAS}}}(Fe^{T_{\text{CAS}}}\Delta T - \Delta T Fe^{T_{\text{CAS}}}) \\
&= e^{-T_{\text{CAS}}}((S + e^{T^{CAS}}F)\Delta T - \Delta T(S + e^{T^{CAS}}F)) \\
&= (F + e^{-T_{\text{CAS}}}S)\Delta T - \Delta T(F + e^{-T_{\text{CAS}}}S) \\
&= F\Delta T - \Delta T F
\end{aligned}
$$

Holds true. This yields

$$
\begin{aligned}
\langle f(t_1) - f(t_2), & t_1 - t_2 \rangle \\
&= \langle \Delta T \Psi_0, e^{-T_{\mathrm{CAS}}}[F, \Delta T]e^{T_{\mathrm{CAS}}}\Psi_0 \rangle + \langle \Delta T \Psi_0, O(t_1) - O(t_2) \rangle \\
&= \langle \Delta T \Psi_0, (F - \Lambda_0)\Delta T \Psi_0 \rangle + \langle \Delta T \Psi_0, O(t_1) - O(t_2) \rangle \\
&\geq \eta \|\Delta T \Psi_0\|_{H^1}^2 - \|\Delta T \Psi_0\|_{H^1}\|O(t_1) - O(t_2)\|_{H^1} \\
&\geq \eta \|\Delta T \Psi_0\|_{H^1}^2 - L\|\Delta T \Psi_0\|_{H^1}\|t_1 - t_2\|_{V_{ext}} \\
&\geq \eta \|\Delta T \Psi_0\|_{H^1}^2 - CL\|\Delta T \Psi_0\|_{H^1}\|\Delta T \Psi_{CAS}\|_{V_{ext}} \\
&\geq \frac{\eta \|\Delta T \Psi_{CAS}\|_{H^1}^2}{\|e^{T^{CAS}}\|_{H^1 \to H^1}^2} - CL\|e^{-T^{CAS}}\|_{H^1 \to H^1}\|\Delta T \Psi_{CAS}\|_{H^1}^2 \\
&= \left(\frac{\eta}{\|e^{T^{CAS}}\|_{H^1 \to H^1}^2} - CL\|e^{-T^{CAS}}\|_{H^1 \to H^1} \right) \|\Delta T \Psi_{CAS}\|_{H^1}^2 \\
&\geq \left(\frac{\eta}{C^2\|e^{T^{CAS}}\|_{H^1 \to H^{-1}}^2} - \frac{L}{C}\|e^{-T^{CAS}}\|_{H^1 \to H^1} \right) \|t_1 - t_2\|_{V_{ext}}^2 \\
&= \gamma \|t_1 - t_2\|_{V_{ext}}^2 \, ,
\end{aligned}
$$
$$(6.46)$$

where in addition to the Lipschitz continuity of O we have used that by Theorem 6.6 the estimate

$$
\|t_1 - t_2\|_{V_{ext}} \leq C\|(T_1 - T_2)\Psi_{CAS}\|_{H^1} \tag{6.47}
$$

holds. $\qquad\square$

In this section we were able to show that under certain assumptions the local version of Zarantonello's theorem is applicable to the tailored coupled cluster function. We emphasise that the here made assumptions are not yet proven to be reasonable. The Lipschitz continuity of the operator O is dependant on the properties of Ψ_{CAS} and therefore of the DMRG solution. The DMRG applied to quantum chemical problems is a non-trivial ansatz and needs detailed knowledge of tensor product approximation methods [49]. The proof of the assumed estimation is therefore left for future studies.

Having established this framework the local version of Zarantonello's theorem is applicable. At the end of this section we show that the tailored coupled cluster method is size consistent. The proof is based on the argumentation used in [2] to show the same result for the coupled cluster method.

Theorem 6.12. *Let H_A and H_B be two independent Hamilton operators for two non-interacting systems A and B i.e. $[H_A, H_B] = 0$. Further be $\Psi_{0,A}$ and $\Psi_{0,B}$ the respective reference states, and $T_A = T_A^{ext} + T_A^{CAS}$ and $T_B = T_B^{ext} + T_B^{CAS}$ the individually calculated cluster operators with the approximate energies E_A and E_B computed by the TCC-method.*

Then $\Psi_{A,B} = e^T \Psi_0 = e^{T_A + T_B}(\Psi_{0,A} \wedge \Psi_{0,B}) = e^{T_A}\Psi_{0,A} \wedge e^{T_B}\Psi_{0,B}$ are the corresponding TCC solution with an approximate energy $E_{A,B} = E_A + E_B$.

Proof. The cluster operator of the dynamic correlation of the super system is given by

$$T_{A,B}^{ext} = \sum_{\mu \in \mathcal{I}_{ext,A} \cup \mathcal{I}_{ext,B}} t_\mu X_\mu \ . \tag{6.48}$$

By definition this cluster operator solves

$$\langle \Psi_\nu, e^{-T_{A,B}^{ext}} e^{-T_{A,B}^{CAS}}(H_A + H_B)e^{T_{A,B}^{ext}} e^{T_{A,B}^{CAS}}\Psi_0 \rangle = 0 \quad , \forall \nu \in \mathcal{I}_{ext,A} \cup \mathcal{I}_{ext,B} \tag{6.49}$$

with $\Psi_0 = \Psi_{0,A} \wedge \Psi_{0,B}$. We introduce the similarity transformed Hamilton operator

$$\tilde{H}_i = e^{-T_i^{CAS}} H_i e^{T_i^{CAS}} \tag{6.50}$$

As $[T_B^{CAS}, T_A^{CAS}] = [T_A^{CAS}, H_B] = [T_{AB}^{CAS}, H_A] = [T_A^{ext}, T_B^{ext}] = 0$ we find

$$\begin{aligned}
e^{-T_{A,B}^{ext}} e^{-T_{A,B}^{CAS}}(H_A + H_B)e^{T_{A,B}^{ext}} e^{T_{A,B}^{CAS}} &= e^{-T_B^{ext}} e^{-T_A^{ext}}(\tilde{H}_A + \tilde{H}_B)e^{T_B^{ext}} e^{T_A^{ext}} \\
&= e^{-T_A^{ext}} \tilde{H}_A e^{T_A^{ext}} + e^{-T_B^{ext}} \tilde{H}_B e^{T_B^{ext}}
\end{aligned} \tag{6.51}$$

which implies

$$0 = \langle \Psi_\nu, e^{-T_A^{ext}} \tilde{H}_A e^{T_A^{ext}} \Psi_{0,A} \rangle + \langle \Psi_\nu, e^{-T_B^{ext}} \tilde{H}_B e^{T_B^{ext}} \Psi_{0,B} \rangle \tag{6.52}$$

Hence,

$$e^{T_{A,B}^{ext}} e^{T_{A,B}^{CAS}} \Psi_0 = e^{T_A^{ext}} e^{T_A^{CAS}} \Psi_{0,A} \wedge e^{T_B^{ext}} e^{T_B^{CAS}} \Psi_{0,B} \ . \tag{6.53}$$

For the energy $E_{A,B}$ we test with the function Ψ_0. We find

$$\begin{aligned}
E_{A,B} &= \langle \Psi_0, (H_A + H_B)\Psi_0 \rangle = \langle \Psi_0, (H_A + H_B)(e^{T_A^{ext}} e^{T_A^{CAS}}\Psi_{0,A} \wedge e^{T_B^{ext}} e^{T_B^{CAS}}\Psi_{0,B}) \rangle \\
&= \langle \Psi_{0,A}, H_A e^{T_A^{ext}} e^{T_A^{CAS}}\Psi_{0,A} \rangle + \langle \Psi_{0,B}, H_B e^{T_B^{ext}} e^{T_B^{CAS}}\Psi_{0,B}) \rangle = E_A + E_B
\end{aligned} \tag{6.54}$$

which proves the size-consistency of the *TCC*. $\qquad\square$

Hence, the tailored coupled cluster method provides correct dissociation energies.

6.2 Tailored-Coupled-Cluster-Single-Double (TCCSD)

As the tailored coupled cluster method is directly derived from the projected coupled cluster method it inherits the bad scaling of the number of amplitude equations $\sharp\mathcal{I}_{ext}$. To quantify $\sharp\mathcal{I}_{ext}$ we recall that the complete active space part of

the set of spin orbitals is chosen to consist out of a small number of amplitudes compared to the total number of spin orbitals. Therefore $\sharp\mathcal{I}_{ext}$ scales close to $\mathcal{O}(K^N)$ which becomes prohibitively large for increasing N. Hence, in practice we approximate the tailored coupled cluster solution with an ansatz containing less parameters $L \ll \sharp\mathcal{I}_{ext}$ by choosing a subset $\mathcal{I}_{h,ext} \subseteq \mathcal{I}_{ext}$ with $L = \sharp\mathcal{I}_{h,ext}$. Analogously to the projected coupled cluster method this is done by truncating the cluster amplitudes with respect to their excitation rank. In later parts of this section we present characteristics of the tailored coupled cluster single double method (TCCSD) where

$$\mathcal{I}_{2,ext} = \{\mu \in \mathcal{I}_{ext} \mid \sharp\mu \leq 2\} \ . \tag{6.55}$$

We point out that the description of the truncated tailored coupled cluster is done equivalently to the projected coupled cluster method.

Subsequently we discuss the equivalence of linked and unlinked tailored coupled cluster equations.

Theorem 6.13. *Be $T_1^{ext} = 0$. Then the linked and unlinked tailored coupled cluster equations are equivalent.*
Linked equations:

$$\begin{cases} E = \langle \Psi_0, e^{-T} H e^T \Psi_0 \rangle \\ 0 = \langle \Psi_\mu, e^{-T} H e^T \Psi_0 \rangle , \quad \mu \in \mathcal{I}ext \ . \end{cases} \tag{6.56}$$

Unlinked equations

$$\begin{cases} E = \langle \Psi_0, H e^T \Psi_0 \rangle \\ E \langle \Psi_\mu, e^T \Psi_0 \rangle = \langle \Psi_\mu, H e^T \Psi_0 \rangle , \quad \mu \in \mathcal{I}_{ext} \ . \end{cases} \tag{6.57}$$

Proof. We consider the tailored coupled cluster method with only single and double excitations into the virtual orbitals. Therefore the excited projection manifold comprises the full set of all singly and doubly excited determinants which are not contained in the complete active space. These states can be characterised with the following sets. The singly excited states are given by

$$\left\{ \Psi \in \mathcal{V}_K \mid \Psi = a_\alpha^\dagger a_i \Psi_0, \ i \in \text{occ}, \ \alpha \in \text{ext} \right\} \ . \tag{6.58}$$

The doubly excited states are given by

$$\left\{ \Psi \in \mathcal{V}_K \mid \Psi = a_\alpha^\dagger a_\beta^\dagger a_i a_j \Psi_0, \ i,j \in \text{occ}, \ \alpha,\beta \in \text{ext} \right\} \tag{6.59}$$

and

$$\left\{ \Psi \in \mathcal{V}_K \mid \Psi = a_\alpha^\dagger a_\beta^\dagger a_i a_j \Psi_0, \ i,j \in \text{occ}, \ \alpha \in \text{ext}, \ \beta \in \text{CAS} \right\} \ . \tag{6.60}$$

In the following, we referee to these sets as

$$\mathcal{I}_h := \{\nu \in \mathcal{I} \mid \sharp\nu \leq 2, \ \nu \notin \mathcal{I}_{CAS}\} \ . \tag{6.61}$$

As the number of electrons is fixed the cluster operator T is described by $T = T_1 + ... + T_N$. As the ansatz space is limited to single and double excitations into the external orbitals the important operators are

$$T_1 = \sum_{\nu \in \mathcal{I}_{CAS}} t_\nu X_\nu + \sum_{\nu \in \mathcal{I}_{ext}} t_\nu X_\nu \quad , \sharp\nu = 1 \tag{6.62}$$

and

$$T_2 = \sum_{\nu \in \mathcal{I}_{CAS}} t_\nu X_\nu + \sum_{\nu \in \mathcal{I}_{ext}} t_\nu X_\nu \quad , \sharp\nu = 2 \ . \tag{6.63}$$

We now define the corresponding matrix representation

$$\mathbf{T} = (T)_{\mu,\nu \in \mathcal{I}_h} \in \mathbb{R}^{\sharp\mathcal{I}_h \times \sharp\mathcal{I}_h} \tag{6.64}$$

with

$$T_{\mu,\nu} = \langle \Psi_\mu, e^T \Psi_\nu \rangle = \langle \Psi_\mu, \Psi_\nu \rangle + \langle \Psi_\mu, T\Psi_\nu \rangle + \frac{1}{2}\langle \Psi_\mu, T^2\Psi_\nu \rangle + ... \tag{6.65}$$

As T only increases the excitation rank this matrix has an upper triangular shape. Due to the orthonormality of the states the diagonal consists out of ones. This structure is depicted in the following block representation Fig. 6.1.

	0 (HF)	S (EXT)	D (EXT)	D (¬CAS)
HF	1	0	0	0
S (EXT)	T_1^{ext}	1	0	0
D (EXT)	T_2^{ext}	T_1^{ext}	1	0
D (¬CAS)	T^2	T_1^{CAS}	0	1

Figure 6.1: Block representation of T.

Due to its triangular shape, the matrix $\mathbf{T}$ is not singular. We now assume that the linked equations hold true. As the matrix $\mathbf{T}$ is not singular the linked equations

are equivalent to

$$A_\mu := \sum_{\nu \in \mathcal{I}_h} T_{\mu,\nu} \left\langle \Psi_\nu, e^{-T} H e^T \Psi_0 \right\rangle = \sum_{\nu \in \mathcal{I}_h} \left\langle \Psi_\mu, e^T \Psi_\nu \right\rangle \left\langle \Psi_\nu, e^{-T} H e^T \Psi_0 \right\rangle$$

$$\underset{(1)}{=} \sum_{\nu \in \mathcal{I}_h} \mathcal{R}(\Psi_\mu)(e^T \Psi_\nu) \mathcal{R}(\Psi_\nu)(e^{-T} H e^T \Psi_0)$$

$$\underset{(2)}{=} \left(\mathcal{R}(\Psi_\mu) \circ e^T \right) \left(\sum_{\nu \in \mathcal{I}_h} \Psi_\nu \mathcal{R}(\Psi_\nu)(e^{-T} H e^T \Psi_0) \right)$$

$$= 0 \tag{6.66}$$

for all $\mu \in \mathcal{I}_h$.

Due to the orthogonality of the state functions the identity on $\mathcal{V}_K$ can be written as

$$I = \sum_{\nu \in CAS} \Psi_\nu \mathcal{R}(\Psi_\nu) + \sum_{\nu \in \mathcal{I}_h} \Psi_\nu \mathcal{R}(\Psi_\nu) + \Psi_0 \mathcal{R}(\Psi_0) \tag{6.67}$$

which is equivalent to

$$\sum_{\nu \in \mathcal{I}_h} \Psi_\nu \mathcal{R}(\Psi_\nu) = I - \sum_{\nu \in CAS} \Psi_\nu \mathcal{R}(\Psi_\nu) - \Psi_0 \mathcal{R}(\Psi_0) . \tag{6.68}$$

This yields

$$0 = A_\mu = \left(\mathcal{R}(\Psi_\mu) \circ e^T \right) (e^{-T} H e^T \Psi_0) \tag{6.69a}$$

$$- \left(\mathcal{R}(\Psi_\mu) \circ e^T \right) \left(\sum_{\nu \in CAS} \Psi_\nu \mathcal{R}(\Psi_\nu)(e^{-T} H e^T \Psi_0) \right) \tag{6.69b}$$

$$- \left(\mathcal{R}(\Psi_\mu) \circ e^T \right) (\Psi_0 \mathcal{R}(\Psi_0)(e^{-T} H e^T \Psi_0)) . \tag{6.69c}$$

We start by analysing Eq. (6.69a). We find

$$\left(\mathcal{R}(\Psi_\mu) \circ e^T \right) (e^{-T} H e^T \Psi_0) = \left\langle \Psi_\mu, e^T e^{-T} H e^T \Psi_0 \right\rangle = \left\langle \Psi_\mu, H e^T \Psi_0 \right\rangle . \tag{6.70}$$

For Eq. (6.69c) we obtain

$$\left(\mathcal{R}(\Psi_\mu) \circ e^T \right) (\Psi_0 \mathcal{R}(\Psi_0)(e^{-T} H e^T \Psi_0)) = \mathcal{R}(\Psi_0)(e^{-T} H e^T \Psi_0) \left(\mathcal{R}(\Psi_\mu) \circ e^T \right) (\Psi_0)$$

$$= \underbrace{\left\langle \Psi_0, e^{-T} H e^T \Psi_0 \right\rangle}_{=E} \left\langle \Psi_\mu, e^T \Psi_0 \right\rangle$$

$$= E \left\langle \Psi_\mu, e^T \Psi_0 \right\rangle . \tag{6.71}$$

For Eq. (6.69b) we find

$$\left(\mathcal{R}(\Psi_\mu) \circ e^T \right) \left(\sum_{\nu \in CAS} \Psi_\nu \mathcal{R}(\Psi_\nu)(e^{-T} H e^T \Psi_0) \right) = \sum_{\nu \in CAS} \left\langle \Psi_\mu, e^T \Psi_\nu \right\rangle \left\langle \Psi_\nu, e^{-T} H e^T \Psi_0 \right\rangle . \tag{6.72}$$

We are taking a closer look at the first scalar product in Eq. (6.72). The definition of the exponential function yields

$$\langle \Psi_\mu, e^T \Psi_\nu \rangle = \langle \Psi_\mu, \Psi_\nu \rangle + \langle \Psi_\mu, T\Psi_\nu \rangle + \frac{1}{2} \langle \Psi_\mu, T^2 \Psi_\nu \rangle + \dots . \qquad (6.73)$$

As $\Psi_\nu \in CAS$ the first term is always equal to zero. Assuming that $\sharp \mu = 1$ all terms are equal to zero as the operator T only increases the degree of excitation. If $\sharp \mu = 2$ there exists an operator such that $\Psi_\mu = T\Psi_\nu$. This can be seen as follows. We consider the case $\Psi_\mu = a_\alpha^\dagger a_\beta^\dagger a_i a_j \Psi_0$ with $\alpha \in \text{ext}$, $\beta \in \text{CAS}$ and $i, j \in \text{occ}$. For $\Psi_\nu = a_\beta^\dagger a_i \Psi_0$ with $\beta \in \text{CAS}$ and $i \in \text{occ}$ we obtain that $\Psi_\mu = a_\alpha^\dagger a_j \Psi_\nu$. As $a_\alpha^\dagger a_j$ is an element of T_1^{ext} which was supposed to zero the contribution of these state functions is zero. For the case that $\Psi_\mu = a_\alpha^\dagger a_\beta^\dagger a_i a_j \Psi_0$ with $\alpha, \beta \in \text{ext}$ and $i, j \in \text{occ}$ the contribution is also zero as the operator $\mathbf{T}$ only increases the degree of excitation. This yields

$$\left(\mathcal{R}(\Psi_\mu) \circ e^T \right) \left(\sum_{\nu \in CAS} \Psi_\nu \mathcal{R}(\Psi_\nu)(e^{-T} H e^T \Psi_0) \right) = \sum_{\nu \in CAS} \langle \Psi_\mu, e^T \Psi_\nu \rangle \langle \Psi_\nu, e^{-T} H e^T \Psi_0 \rangle$$

$$= 0 .$$

$$(6.74)$$

We conclude

$$0 = A_\mu = \langle \Psi_\mu, H e^T \Psi_0 \rangle$$
$$- 0$$
$$- E \langle \Psi_\mu, e^T \Psi_0 \rangle$$
$$\Leftrightarrow \quad E \langle \Psi_\mu, e^T \Psi_0 \rangle = \langle \Psi_\mu, H e^T \Psi_0 \rangle$$

$$(6.75)$$

which was the claim. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\square$

Having proven this equivalence of the linked and unlinked coupled cluster equations we are able to show that the amplitude equations for the tailored coupled cluster single double method follow a certain structure. We find as a consequence of Theorem 3.11, the Slater–Condon rules, the following theorem.

Theorem 6.14. *The solution of TCCSD does not depend on $T_k^{(cas)}$ for $k > 3$.*

Proof. Analogously to the previous proof we consider the tailored coupled cluster method with only single and double excitations into the virtual orbitals. The main tools of this proof are the Slater-Condon rules. Subsequently, we consider two different cases depending on the level of excitation of the test function Ψ_μ.

Singly excited states Ψ_μ**:** As the Slater-Condon rules state that the considered state function can only differ in an excitation upto the excitation rank two. Hence, the unlinked tailored coupled cluster equations become of the form

$$
\begin{aligned}
0 =& \langle \Psi_\mu, (H-E)\Psi_0 \rangle + \langle \Psi_\mu, (H-E)\frac{1}{2}T_2^{ext}T_1^{CAS}\Psi_0 \rangle + \langle \Psi_\mu, (H-E)T_2^{ext}\Psi_0 \rangle \\
&+ \langle \Psi_\mu, (H-E)T_1^{CAS}\Psi_0 \rangle + \langle \Psi_\mu, (H-E)T_2^{CAS}\Psi_0 \rangle \\
&+ \langle \Psi_\mu, (H-E)\frac{1}{2}\left(T_1^{CAS}\right)^2\Psi_0 \rangle \, .
\end{aligned}
$$
(6.76)

Doubly excited states Ψ_μ**:** Analogously to the first case we find

$$
\begin{aligned}
0 =& \langle \Psi_\mu, (H-E)\Psi_0 \rangle + \langle \Psi_\mu, (H-E)T_1^{CAS}\Psi_0 \rangle + \langle \Psi_\mu, (H-E)T_2^{ext}\Psi_0 \rangle \\
&+ \langle \Psi_\mu, (H-E)\frac{1}{2}\left(T_1^{CAS}\right)^2\Psi_0 \rangle + \langle \Psi_\mu, (H-E)T_2^{CAS}\Psi_0 \rangle \\
&+ \langle \Psi_\mu, (H-E)\frac{1}{2}T_2^{ext}T_1^{CAS}\Psi_0 \rangle + \langle \Psi_\mu, HT_3^{CAS}\Psi_0 \rangle \\
&+ \langle \Psi_\mu, (H-E)\frac{1}{2}\left(T_2^{ext}\right)^2\Psi_0 \rangle + \langle \Psi_\mu, (H-E)\frac{1}{2}T_2^{ext}T_2^{CAS}\Psi_0 \rangle \, .
\end{aligned}
$$
(6.77)

We see that the $TCCSD$ solution does not depend on cluster operators with an excitation rank higher that than three. Hence, it follows the claim. $\qquad\square$

Considering the case in which single excitation cluster amplitudes are equal to zero we find that the unlinked tailored coupled cluster equations become of a simpler form.

Remark 6.15. *For $T_1^{CAS} = 0$ the unlinked tailored coupled cluster equations become*

$$
\begin{aligned}
0 =& \langle \Psi_\mu, (H-E)\Psi_0 \rangle + \langle \Psi_\mu, (H-E)T_2^{ext}\Psi_0 \rangle + \langle \Psi_\mu, (H-E)T_2^{CAS}\Psi_0 \rangle \\
&+ \langle \Psi_\mu, (H-E)T_3^{CAS}\Psi_0 \rangle + \langle \Psi_\mu, (H-E)\frac{1}{2}\left(T_2^{ext}\right)^2\Psi_0 \rangle \\
&+ \langle \Psi_\mu, (H-E)\frac{1}{2}T_2^{ext}T_2^{CAS}\Psi_0 \rangle \, .
\end{aligned}
$$
(6.78)

W point out that the assumption of $T_1^{ext} = T_1^{CAS} = 0$ is not unrealistic as for example the use of Brueckner orbitals [3, 4, 5] or an orbital-adaptive coupled-cluster method [6] yield that the cluster amplitudes for single excitations are equal to zero.

7 Conclusion

For decades the coupled cluster method had been existing without any mathematical foundations. It was only in 2009 that the mathematical community became interested in developing rigorous models for this formalism [2, 47, 48]. The analysis of the projected coupled cluster method presented by Schneider [2] was, like this thesis, restricted to the finite dimensional case. In the following years Rohwedder and Schneider developed a more general framework for the infinite dimensional problem, namely the continuous coupled cluster formulation [47, 48].

Inspired by this mathematical approach to analyse quantum chemical methods we attacked the tailored coupled cluster method in a similar way. Even thought the mathematical formulation of the TCC method as a non-linear Galerkin scheme was directly transferable from Schneider's work [2] by introducing a basis splitting, the generalisation of the analysis required several modifications:

The generalisation of the HOMO-LUMO gap to the CAS-EXT gap weakened the upper bound of $\varepsilon_\nu/\varepsilon_\mu$ as it turned out to be impossible to ensure it for all excitation indices in $\mathcal{I}$. The correction was to introduce different bounds depending on the excitation index μ.

Also the generalisation of the local strong monotonicity of the TCC function f had stronger assumptions on the Baker–Campbell–Hausdorff expansion of the fluctuation operator Eq. (6.42) as a consequence. In the projected coupled cluster case the Gårding estimate dictated the condition on the Lipschitz constant for the respective expansion. For the tailored coupled cluster function it is not only the Gårding constant that influences the upper bound but also the operator norm of the CAS-CI solution's cluster operator. It remains to investigate how realistic this strong condition on the Lipschitz constant is, especially for the case of a CAS-CI solution extracted from the DMRG.

Having overcome these obstacles we were able to use a local version of Zarantonello's theorem and to show locally unique solutions with a quasi optimal error estimate $\|x_* - x_d\| \leq L/\gamma d(x_*, X_d)$ for the tailored coupled cluster function.

Due to the reduction of computational costs and the fact that for dynamical elec-

tron correlations it is mostly the first and second order excitation amplitudes that determine the state function, the CCSD is the most used coupled cluster method. This motivated our investigation on how the TCC method behaves under truncation of excitation amplitudes. The mayor difference to the CCSD method is that for the TCCSD method the linked and unlinked amplitude equations are not equivalent. This is a consequence of existing mixed excitations, i.e. excitations into the CAS- as well as into the EXT-space. The projection of these mixed states onto $CAS^{\perp}$ yields non-zero overlap integrals which can only be fixed by setting the single excitation amplitudes equal to zero. This is guaranteed by using approaches like Brueckner orbitals [3, 4, 5] or an orbital-adaptive coupled-cluster method [6].

Looking at the computational costs it is also interesting to do further investigations in the direction of linearised coupled cluster method. The articles [50] and [51] show computational results for linearised coupled cluster approaches in the multi-reference methods and also in combination with matrix product states. Analysing this linearised coupled cluster approach in combination with the presented DMRG-TCC method seems to us very promising.

Concluding, the density matrix renormlisation group tailored coupled cluster method is an extremely promising multi-reference method [1]. We are convinced that this thesis forms the backbone of subsequent analysis in the spirit of the continuous coupled cluster formulation [47, 48] but also for further computational approaches in the externally corrected coupled cluster regime in the spirit of [50, 51].

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