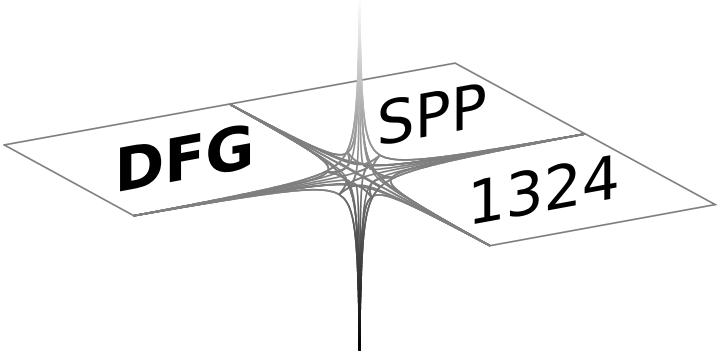
DFG-Schwerpunktprogramm 1324

„Extraktion quantifizierbarer Information aus komplexen Systemen”

The Continuous Coupled Cluster Formulation for the Electronic Schrödinger Equation

T. Rohwedder

Preprint 97



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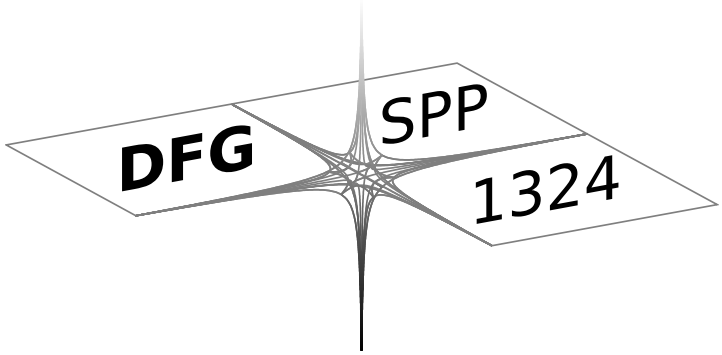

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THE CONTINUOUS COUPLED CLUSTER FORMULATION FOR THE ELECTRONIC SCHRÖDINGER EQUATION*

Thorsten Rohwedder[1]

Abstract. Nowadays, the Coupled Cluster (CC) method is the probably most widely used high precision method for the solution of the main equation of electronic structure calculation, the *stationary electronic Schrödinger equation*. Traditionally, the equations of CC are formulated as a nonlinear approximation of a Galerkin solution of the electronic Schrödinger equation, i.e. within a given discrete subspace. Unfortunately, this concept prohibits the direct application of concepts of nonlinear numerical analysis to obtain e.g. existence and uniqueness results, quasi-optimality estimates, or results on the convergence of discrete solutions to the full solution. Here, this shortcoming is approached by showing that the original, continuous electronic Schrödinger equation can under suitable assumptions be formulated equivalently as a root equation for an infinite-dimensional nonlinear Coupled Cluster operator, discretizations of which then lead to the canonical projected CC equations. As the main step, continuity properties of the cluster operator T and its adjoint as mappings on the antisymmetric energy space $\mathbb{H}^1$ are established.

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1. Introduction

The Coupled Cluster (CC) approach was derived around 1960 in the field of atomic physics [17,18,33,55], and later introduced in the context of quantum chemistry (see [16]). It is today the probably most widely applied tool in the calculation of ground state solutions of the stationary N-electron Schrödinger equation when high-accuracy results

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are demanded. In the variant of the CCSD(T) method [44], which can be applied to small to medium-sized molecules with reasonable computational effort, CC often provides results which are within the error bars of corresponding practical experiments [38]. CCSD(T) is therefore often referred to as the "golden standard of quantum chemistry".

The ground state problem for the electronic Schrödinger equation, for the numerical treatment of which the CC method is used, governs the physical behaviour of N electrons in the Coulomb field of a fixed set of nuclei, see [28, 52, 57] for some main results. To admit for a sensible discretization and a mathematically sound algorithmic treatment, it is in the context of numerical analysis best phrased as a weak operator eigenproblem for an eigenfunction $\underline{\Psi}$ describing the electronic ground state [57], i.e. "Find $\underline{\Psi} \in \mathbb{H}^1$ and $E \in \mathbb{R}$ such that

$$\langle \Phi,\ H\underline{\Psi} \rangle \ = \ E\langle \Phi,\ \underline{\Psi} \rangle \ \text{ for all } \Phi \in \mathbb{H}^1, \tag{1.1}$$

and such that E is the lowest eigenvalue of H." In this, the solution space $\mathbb{H}^1$ is a suitable energy (Sobolev) space consisting of antisymmetric functions, and the operator $H : \mathbb{H}^1 \to \mathbb{H}^{-1}$ is the weak N-electron Hamiltonian, mapping to the dual space of $\mathbb{H}^1$ (see Sec.2). To treat the Schrödinger equation (1.1) in the way the CC method is canonically used (see e.g. the quantum chemical standard work [26]), three steps are taken:

(a) Galerkin discretization of (1.1): Restriction to a discrete subspace $\mathbb{H}^1_d$ gives a (usually extremely high-dimensional) discrete eigenvalue problem for a function $\underline{\Psi}_d \in \mathbb{H}^1_d$,

$$\langle \Phi_d,\ H\underline{\Psi}_d \rangle \ = \ E_d\langle \Phi_d,\ \underline{\Psi}_d \rangle \text{ for all } \Phi_d \in \mathbb{H}^1_d. \tag{1.2}$$

By quantum chemists, $\underline{\Psi}_d$ is called the "full Configuration Interaction (full CI) solution" of the discrete system (1.2).

(b) In a second step, the full-CI equation is equivalently re-parametrized by an exponential ansatz as follows: From a preliminary Hartree-Fock calculation (see e.g. [26]), one has an often rather good rank-1-approximation Ψ_0 to the sought solution $\underline{\Psi}_d$ at hand. $\underline{\Psi}_d$ is then written as a so-called excitation of the reference solution Ψ_0,

$$\underline{\Psi}_d \ = \ (I + S)\Psi_0,$$

in which S is the so-called *cluster operator* of $\underline{\Psi}_d$ that maps the reference Ψ_0 to the sought correction $\Psi^* = \underline{\Psi}_d - \Psi_0$ (see Sec. 2 for the exact definition). Ψ_0 fixed, solution of (1.2)

is thus equivalent to the computation of a cluster operator S such that

$$\langle \Phi_d,\ H(I+S)\Psi_0\rangle \ =\ E_d\langle \Phi_d,\ (I+S)\Psi_0\rangle \text{ for all } \Phi_d \in \mathbb{H}^1_d. \tag{1.3}$$

By standard matrix algebra (see e.g. [50, 55]), every cluster operator of the form $I+S$ can also be expressed as the exponential of a cluster operator T, so that (1.3) can in a second step be rephrased as determination of T such that

$$\langle \Phi_d, He^T\Psi_0\rangle \ =\ E_d\langle \Phi_d,\ e^T\Psi_d\rangle \text{ for all } \Phi_d \in \mathbb{H}^1_d, \tag{1.4}$$

or alternatively, because e^{-T} is invertible, as the solution of

$$\langle \Phi_d, e^{-T}He^T\Psi_0\rangle \ =\ E_d\langle \Phi_d,\ \Psi_0\rangle \text{ for all } \Phi_d \in \mathbb{H}^1_d. \tag{1.5}$$

for T. These are the nonlinear "full-CC" equations (1.5) which are equivalent to the "full-CI"-formulation (1.2) on the space $\mathbb{H}^1_d$, and which define a nonlinear root equation for a coefficient vector of so-called *cluster amplitudes* $(t_\alpha)_{\alpha\in\mathcal{I}}$ determining T. In contrast to the terms occurring in (1.4), (1.5) can be evaluated exactly [20, 26, 46] and is therefore the formulation almost exclusively used in practice.

(c) In a final step, only certain of the amplitudes t_α determining T are used in the calculation. This corresponds to a further reduction of the test space $\mathbb{H}^1_d$ to a subspace $\mathbb{H}^1_D$, usually pushing practically relevant problems into the range of computability. The result is a reduced set of CC equations

$$\langle \Phi_D, e^{-T}He^T\Psi_0\rangle \ =\ E_D\langle \Phi_D,\ \Psi_0\rangle \qquad \text{for all } \Phi_D \in \mathbb{H}^1_D. \tag{1.6}$$

The selection criteria for basis functions included in the calculation normally base on the so-called "excitation level" of the basis functions, leading then e.g. to the often used Coupled Cluster Singles Doubles (CCSD) equations. In practice, the resulting equations are then evaluated with the aid of the Second Quantization formalism (see [20] for a comprehensible treatment) and then usually solved by Newton-type methods [26], often enhanced by the DIIS acceleration method [47].

In contrast to (1.5), the equations (1.6) are no longer equivalent to the CI (Galerkin) discretization of (1.1) on $\mathbb{H}^1_D$, but preferrable over the CI method due to various favourable properties: The CC method enjoys a wide range of applicability in a black-box style and converges quickly and systematically to the full-CI energy limit E_d when applied to relatively well-behaved systems as typically C-H-chains, rings, alcohols, cetones and

aminoacids are. It also usually outperforms the correspondingly truncated CI method, see e.g. [19,31]. As another important feature truncated CC has, in contrast to truncated CI methods, the property of being size-consistent [4,6,40], making CC the tool of choice when describing reaction mechanisms. For a review on Coupled Cluster theory, the reader is referred to [5,34] and the abundance of references given therein, as well as to the article [10] for a broader scope on the applications in physics; for some recent developments, see [7,14,32,39] as well as the references given in Section 2.

In spite of the CC method's practical utility and popularity, theoretical results from the mathematical point of view are rather scarce. Only recently a first approach has been undertaken in [50], where the approximation properties of the truncation step from the discrete full-CI equations (1.3) to the projected Coupled Cluster equation (1.6) was analyzed. Thus, the problems associated with the direct re-formulation of the original, infinite-dimensional problem (1.1) as an infinite-dimensional nonlinear Coupled Cluster method approached in this work are circumvented; the flipside of this proceeding is that the results do not allow for direct estimates with respect to the true solution $\underline{\Psi} \in \mathbb{H}^1$, and convergence to $\underline{\Psi}$ can only be proved under certain uniformity assumptions for the discrete equations. Also, the approach *a priori* excludes the analysis of methods where the size of the underlying one-particle basis is varied. The latter are of interest in the context of error estimation though, especially in view of the fact that convergence of different CC models towards the limit within the full CI-space usually is rather fast, while the convergence of the full-CI solutions $\underline{\Psi}_d \in \mathbb{H}^1_d$ to the continuous limit $\underline{\Psi} \in \mathbb{H}^1$ is often rather slow with respect to the size of the underlying one-particle basis set. As a first step, the goal of this work is to show that under suitable assumptions, the electronic Schrödinger equation (1.1) can in a mathematically rigorous fashion be *equivalently* re-formulated as Coupled Cluster equations in a coefficient space reflecting the continuous space $\mathbb{H}^1$. The resulting method will be termed "the continuous Coupled Cluster method", consisting in finding a suitably defined cluster operator T such that

$$\langle \Phi, e^{-T} H e^{T} \Psi_0 \rangle = E^* \langle \Phi, \Psi_0 \rangle \text{ for all } \Phi \in \mathbb{H}^1. \tag{1.7}$$

The step of globalizing the canonical CC formulation of the CI problem (1.2) to a continuous CC formulation of the original problem (1.1) consists in three steps, that will be taken care of in the following Sections 2 to 4:

(i) The formalism of cluster operators, defined by their action on a fixed tensor basis set, has to be adapted to the infinite dimensional space appropriately. The analysis of finite-dimensional CC theory uses the existence of a suitable one-particle operator F, for instance a Fock or Kohn-Sham operator, that admits for an N-dimensional invariant subspace (N being the number of electrons), a basis of which is used to define the reference Ψ_0 and the cluster operators. In Section 2, we introduce an according assumption, which may loosely be described as the existence of a Fock-style one-particle operator having a ground state. In many cases, this assumption is fulfilled by according continuous Fock or Kohn-Sham operators. As well, it covers many of the more sophisticated CC methods used in practice. We also briefly review the necessary parts of the ample mathematical background that underlies the electronic Schrödinger equation [27, 45, 54, 57] and its formulation in terms of cluster operators in the energy space $\mathbb{H}^1$.

(ii) The critical point in the formulation of (1.7) is from the point of view of functional analysis that the cluster operators T as well as their L_2-adjoints $T^\dagger$ now have to be bounded mappings on the energy space, $T : \mathbb{H}^1 \to \mathbb{H}^1$, to make the continuous method well-defined. To verify this property, there are to our knowledge no suitable concepts available in the literature so far. The idea of the present proof given in Section 3 is mainly based on the above mentioned existence of a suitable reference ground state, together with the nilpotency properties of annihilation and creation operators which allows to reduce the analysis to finite-dimensional ℓ_p-estimates [50] with the constants depending only on the number N of electrons.

(iii) These properties once verified, application of well-known Banach algebra theory can be used to supply the remaining ingredients for formulation of the continuous CC equations and the continuous CC function f; this step is taken in Section 4.

In a follow-up publication [48], we will then harvest the continuous CC formulation to directly derive from it existence and uniqueness results for the continuous and discrete equations and to obtain quasi-optimality estimates and error estimators for the energies calculated by CC. The analysis will also underpin the importance of particular contants (as the quality of the reference determinant Ψ_0 and spectral gaps of the Hamiltonian) for the practical convergence behaviour of the Coupled Cluster method.

2. A setting for the continuous CC equations

This section, building up the necessary theoretical background for the continuous CC equations, starts by reformulating the electronic Schrödinger equation (1.1) in its intermediate normalization formulation that is commonly used in post-Hartree-Fock calculations and sometimes termed the complete Configuration Interaction formulation (as in contrast to the discrete full CI-formulation (1.2)) in the context of quantum chemistry. The main assumption, which may loosely be described as the existence of a Fock-style one-particle operator having a ground state, is fixed in Assumption 2.1; we then define cluster operators in Section 2.2.

2.1. **The complete-CI formulation of the electronic Schrödinger equation.**

The solution space $\mathbb{H}^1$ on which the N-particle electronic Schrödinger equation is formulated combines two requirements on the solution Ψ, namely that it be contained in the Sobolev space [49] $H^1\big((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N\big)$ of finite kinetic energy, and that it be subject to the *Pauli principle*, according to which the wave function has to be antisymmetric (i.e. sign-changing) under every permutation of two non-identical particle coordinates $(x_i, s_i), (x_j, s_j) \in \mathbb{R}^3 \times \{\pm\frac{1}{2}\}$. Denoting the subspace of antisymmetric functions contained in $L^2((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N)$ by $\mathbb{L}^2$, the solution space is given by

$$\mathbb{H}^1 := \mathbb{L}^2 \cap H^1\big((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N\}\big). \tag{2.1}$$

On this space, we are looking for solutions of the electronic Schrödinger equation. Its weak formulation, a convenient starting point for numerical treatment, is formulated in terms of the bounded, coercive [57] bilinear form $h : \mathbb{H}^1 \times \mathbb{H}^1 \to \mathbb{R}$ on the energy space $\mathbb{H}^1$, induced by the strong Hamiltonian $\hat{H} : \mathbb{H}^2 \to \mathbb{L}^2$ [27, 45, 52, 56],

$$h(\Psi, \Psi') := \langle \nabla\Psi, \nabla\Psi' \rangle \; + \; \langle \Psi, \big(\sum_{i=1}^{N} \sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{1}{|x_i - x_j|} \; - \; \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k}{|x_i - R_k|} \big) \Psi' \rangle. \tag{2.2}$$

In this $\langle \cdot, \cdot \rangle$ denotes the usual $L^2((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N)$-inner product, the velocity operator ∇ acts on every spatial component of a wave function Φ, and the constants $Z_k \in \mathbb{N}$, $R_k \in \mathbb{R}^3$ are the charges and positions of the fixed nuclei. The solutions of the weak eigenvalue equation

$$h(\Psi, \cdot) \; = \; E\langle \Psi, \cdot \rangle \quad \text{in} \quad \mathbb{H}^{-1}, \tag{2.3}$$

correspond to the eigenfunctions of the classical, unbounded Hamiltonian $\widehat{H} : \mathbb{H}^2 \to \mathbb{L}^2$ [57]. By standard functional analysis, (2.3) can be restated as operator eigenvalue equation for a weak Hamiltonian $H : \mathbb{H}^1 \to \mathbb{H}^{-1}$,

$$\langle H\underline{\Psi}, \cdot \rangle \;:=\; h(\underline{\Psi}, \cdot) \;=\; E\langle \underline{\Psi}, \cdot \rangle \quad \text{in} \quad \mathbb{H}^{-1},$$

leading to the equation (1.1) formulated at the beginning of this work.

Using linearity, (1.1) can be replaced by a globalized Fourier ansatz, i.e. testing the functional (2.2) with all elements Ψ_μ of a basis of the space $\mathbb{H}^1$. Given a complete *one-particle* basis

$$B \;:=\; \{\psi_P \mid P \in \mathcal{I}\}$$

of the one-electron state space

$$H^1 \;:=\; H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$$

indexed by ordered an set $\mathcal{I}$, a *Slater basis* of the antisymmetric space $\mathbb{H}^1$ is given by

$$\mathbb{B} \;:=\; \{\Psi_\mu \mid \mu \in \mathcal{M}\}, \qquad \Psi_\mu \;:=\; \bigwedge_{i=1}^{N} \chi_{P_i} \;:=\; \mathcal{Q}(\otimes_{i=1}^{N} \chi_{P_i})$$

where $\mathcal{Q} : L^2((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N) \to \mathbb{L}^2$ is the antisymmetrization mapping, defined by its action on functions $\Psi = \Psi((x_1, s_1), \ldots, (x_N, s_N))$ via

$$\mathcal{Q}\Psi = \frac{1}{\sqrt{N!}} \sum_{\pi \in S(N)} (-1)^{\mathrm{sgn}(\pi)} \Psi((x_{\pi(1)}, s_{\pi(1)}), \ldots, (x_{\pi(N)}, s_{\pi(N)})), \tag{2.4}$$

with the sum running over the permutational group $S(N)$ on N elements operating on the indices of Ψ, and where $\mathcal{M}$ consists of ordered multi-indices,

$$\mathcal{M} = \{(P_1, \ldots, P_N) \mid P_i \in \mathcal{I},\ P_1 < \ldots < P_N\}.$$

In the discretized ("projected") Coupled Cluster method (1.5) in its simplest form, a finite one-particle basis set B_d is provided by d eigenfunctions of the converged discrete Fock operator $F_{HF,d}$ obtained from a preliminary Hartree-Fock calculation, leading to simpler equations and also facilitating the numerical analysis performed in [50]. In the present infinite dimensional setting, the continuous Fock operator $F_{HF} : H^1 \to H^{-1}$ does not allow for a complete eigensystem anymore, so that the analysis from [50] and the formulation of

the Coupled Cluster method do not extend straight-forwardly to the continuous setting. Instead, we we will base our analysis on the following assumption.

Assumption 2.1. *A subset*

$$B_{occ} \;:=\; \{\chi_{I_1}, \ldots, \chi_{I_N}\} \;\subseteq\; B$$

of N basis functions from B is a basis of an N-dimensional invariant subspace of a linear symmetric operator $F : H^1 \to H^{-1}$; this operator F is spectrally equivalent to the canonical H^1-inner product $\langle \cdot, \cdot \rangle_1$, i.e. there are $\gamma, \Gamma > 0$ such that

$$\gamma \;\langle \varphi, \varphi \rangle_1 \;\leq\; \langle F\varphi, \varphi \rangle \;\leq\; \Gamma \;\langle \varphi, \varphi \rangle_1 \quad \textit{for all} \quad \varphi \in H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\}).$$

Remarks on the assumption. Assumption (2.1) can be shown to be fulfilled by the shifted infinite dimensional Fock operator F_{HF} and an according invariant subspace belonging to N lowest eigenvalues of F_{HF} in many practically relevant cases [36, 37], for instance for neutral and positively charged molecules. Under similar assumptions, it has recently been proven for certain Kohn-Sham type operators used in density functional theory [1].[1] Also, any set of N eigenfunctions spanning an invariant subspace S_N of a discrete Fock operator F_d can be complemented by a basis of $S_N^{\perp}$ to fulfil the assumption. This also covers many of the more sophisticated CC schemes which are not directly based on canonical orbitals (i.e. eigenfunctions of the Fock operator) anymore, but use certain localization criteria to rotate the occupied orbitals (to e.g. Foster-Boys-type orbitals [11], Pipek-Mazay-type orbitals [43] or enveloped localized orbitals [3]), use non-orthogonal bases for the complement $B \backslash B_{\mathrm{occ}}$ (e.g. the projected atomic orbitals (PAOs) in the LCCSD approach [25, 51]), or enhance the virtual space obtained from Hartree-Fock calculations by specialized basis functions taking the numerically hazardous electron-electron cusp [24, 29] into account (as e.g. the recent powerful $r_{1,2}$- and $f_{1,2}$- methods [30]). Nevertheless, all of these schemes maintain the orthogonality between B_{occ} and $B \backslash B_{\mathrm{occ}}$ and are therefore covered by the analysis in this publication.

In the language of quantum chemistry, the basis functions $\chi_P \in B$ are termed *spin orbitals*. A spin orbital χ_I from B_{occ} is commonly called *occupied orbital*, and this situation will

[1] That the Fock operator F_{HF} is bounded below and can thus be shifted to a positive operator is a consequence of the Hardy inequality [56, 57] and is essentially the same as for the weak Hamiltonian H given in [57]. The same result holds if for the Kohn-Sham operator if the exchange term maps $H^1(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ boundedly.

be abbreviated by $I \in \mathrm{occ}$. A function $\chi_A \in B \backslash B_{\mathrm{occ}}$ is called *virtual orbital*, denoted by $A \in \mathrm{virt}$. It is also a notational convention that in summations etc., occupied orbitals are labeled by letters $I, J, K, \ldots \in \mathrm{occ}$, virtual orbitals by letters $A, B, C, \ldots \in \mathrm{virt}$, and unspecified orbitals by letters $P, Q, R, \ldots \in \mathcal{I}$. The requirement that F has an invariant N-dimensional subspace translates in this language as

$$\langle F\chi_I, \chi_A \rangle \;=\; \langle \chi_I, \chi_A \rangle \;=\; 0 \qquad \text{for all } I \in \mathrm{occ},\ A \in \mathrm{virt}. \tag{2.5}$$

The ansatzes of (single-reference) Configuration Interaction and Coupled Cluster theory are perturbational in the sense that they assume the existence of a preliminarily calculated *reference determinant*. This reflects in the second, mild assumption.

Assumption 2.2. *The reference Slater determinant*

$$\Psi_0 \;:=\; \bigwedge_{i=1}^{N} \chi_{I_i}, \tag{2.6}$$

approximates the sought eigenfunction $\underline{\Psi}$ *to some extent. In particular, the nonorthogonality assumption*

$$\langle \underline{\Psi}, \Psi_0 \rangle \;\neq\; 0$$

holds.

In practice, this reference mostly is given by the Hartree-Fock solution [15, 26] of the system . Such reference Ψ_0 given, equation (1.1) can now be formulated in terms of the CI ansatz: "Find $\underline{\Psi} = \Psi_0 + \Psi^* \in \mathbb{H}^1$ such that

$$\langle H(\Psi_0 + \Psi^*), \Psi_\mu \rangle \;=\; E\langle \Psi_0 + \Psi^*, \Psi_\mu \rangle \quad \text{for all} \quad \Psi_\mu \in \mathbb{B}, \quad \text{where} \quad \Psi^* \perp \Psi_0." \tag{2.7}$$

In this, the correction Ψ^* is orthogonal to the reference in the $\mathbb{L}_2$-inner product, so that the *intermediate normalization* condition

$$\langle \underline{\Psi}, \Psi_0 \rangle \;=\; 1 \tag{2.8}$$

is fulfilled, and also orthogonal (due to (2.5)) in the inner product induced by the lifted Fock operator

$$F^N : \mathbb{H}^1 \to \mathbb{H}^{-1}, \qquad F^N = \sum_{i=1}^{N} F_i, \qquad F_i = \underbrace{I \otimes \ldots \otimes I}_{i-1 \text{ times}} \otimes F \otimes \underbrace{I \otimes \ldots \otimes I}_{d-i \text{ times}}. \tag{2.9}$$

The inner product induced by F^N is equivalent to that on $\mathbb{H}^1$ [46] and will be denoted by $\langle \cdot, \cdot \cdot \rangle_F$; the corresponding norm is abbreviated by $|| \cdot ||_F$.
Equation (2.7) will now be reformulated in terms of the cluster operators introduced below to derive the CC method.

2.2. **Annihilation and creation operators, excitation operators.**

Various methods in quantum chemistry, including the Coupled Cluster method, are formulated in terms of annihilation and creation operators borrowed the formalism of Second Quantization [8]. Any linear operator on $\mathbb{F}$, in particular the electronic Hamiltonian and the cluster operators of CC theory, may be written as a sum of polynomials in creation and annihilation operators $a_I^\dagger, a_I$ [13]. To define these operators, we will in this paragraph have to utilize the antisymmetric, real valued space $\mathbb{L}^2 = \mathbb{L}^2_N$ for a varying number N of electrons. Therefore, the spaces, operators etc. under consideration will be equipped with an index N indicating the number of particles where needed. Because notations used are intuitive and only needed in this part, they will not be introduced at all length. From the next paragraph on, the particle number N will be fixed again; consequently, the indices will be omitted again. The (fermion) Fock space [23] is defined as

$$\mathbb{F} := \bigoplus_{N=0}^{\infty} \mathbb{L}^2_N,$$

where $\bigoplus$ denotes the direct orthogonal sum of the Hilbert spaces $\mathbb{L}^2_N$. By writing N-electron state vectors $\Psi_N \in \mathbb{L}^2_N$ as $(\delta_{k,N}\Psi_N)_{k\in\mathbb{N}} = (0, 0, \ldots, 0, \Psi_N, 0, \ldots)$, we may embed $\mathbb{L}^2_N$ in $\mathbb{F}$ for any N. Note that the case $N = 0$ is also included in the above definition of the space $\mathbb{F}$. For this case, $\mathbb{L}^2_0$ is (by definition of the tensor product) the underlying field of the complex numbers. This is a one-dimensional vector space, thus containing up to a phase factor only normalized vector called the *vacuum state* $|\rangle$. This state is in some sense the starting point for the formalism of second quantization, as any state vector may be created from it by the use of the creation operators introduced in the following.

Annihilation and creation operators. Motivated by the theory developed below, our definition of creation and annihilation operators acting on $\mathbb{F}$ also allows for non-orthogonal basis sets and functions f not contained in the basis B.

Definition 2.3. *For $1 \leq N \in \mathbb{N}$, $f \in L^2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$ and $\Psi_\mu \in \mathbb{B}_N$, we use the mapping $\mathcal{Q}_{N+1} : L^2\big((\mathbb{R}^3 \times \{\pm\frac{1}{2}\}^{N+1}\big) \to \mathbb{L}^2_{N+1}$ from (2.4) to define*

$$a^\dagger_{f,N}\Psi_\mu \quad := \quad \mathcal{Q}_{N+1}\big(f \otimes \Psi_\mu\big). \tag{2.10}$$

The linear continuation of the above operator to linear combinations is obviously $\mathbb{L}_2$-bounded, and by closing the operator in $\mathbb{L}^2_N$, we obtain a linear map

$$a^\dagger_{f,N} : \mathbb{L}^2_N \to \mathbb{L}^2_{N+1}.$$

For $N = 0$, we let $a^\dagger_{f,0}|\rangle = f \in \mathbb{L}^2_1$. The creation operator *or* creator *of f is now defined on all of $\mathbb{F}$ by*

$$a^\dagger_f : \mathbb{F} \to \mathbb{F},\ a^\dagger_f := \bigoplus_{N=0}^{\infty} a^\dagger_{f,N}. \tag{2.11}$$

In particular, if $f = \chi_P$ from the fixed basis set $\mathbb{B}$, we will denote $a^\dagger_P := a^\dagger_{\chi_P}$ for convenience.

The annihilation operator *or* annihilator $a_f : \mathbb{F} \to \mathbb{F}$ *of f is the adjoint of the creation operator $a^\dagger_f : \mathbb{F} \to \mathbb{F}$ of f. The annihilator of a basis function $\chi_P \in \mathbb{B}$ is denoted by a_P.*

□

Note that because the creation operator $a^\dagger_f$ is closed, the adjoint of the adjoint of $a^\dagger_f$ is $a^\dagger_f$, so that the adjoint of the annihilator a_f is indeed $a^\dagger_f$, as indicated by the notation. Later on, we will need the properties of the annihilation and creation operators compiled in the following lemma. The proofs are generalized from according statements for the finite-dimensional case [26, 53] straightforwardly, so they are omitted here.

Lemma 2.4. *(Properties of the creation and annihilation operators)*

(i) *For $f \in \mathrm{span}\{\chi_{P_1}, \ldots \chi_{P_N}\}$, we have*

$$a^\dagger_f\big(\bigwedge_{n=1}^{N} \chi_{P_n}\big) = 0,$$

and for $f \notin \mathrm{span}\{\chi_{P_1}, \ldots \chi_{P_N}\}$,

$$a_f\big(\bigwedge_{n=1}^{N} \chi_{P_n}\big) = 0,$$

where 0 is the zero vector $0 \in \mathbb{F}$ (not to be confused with the vacuum state).

(ii) *The action of a_f on an N-electron elementary tensor $\Psi = \otimes_{i=1}^N \chi_{P_i}$ is given by*

$$\tilde{a}_f \Psi \quad := \quad \sum_{n=1}^{N} (-1)^{n-1} \langle f, \chi_{P_n} \rangle \; \mathcal{Q}\Big(\big(\otimes_{i=1}^{n-1} \chi_{P_i} \big) \otimes \big(\otimes_{i=n+1}^{N} \chi_{P_i} \big) \Big). \tag{2.12}$$

(iii) *In particular, there holds for $\Psi_\mu = \otimes_{i=1}^N \chi_{P_i} \in \mathbb{B}$ and $P_i \in \{P_1, \ldots, P_N\}$ that*

$$a_{P_i}\big(\bigwedge_{n=1}^{N} \chi_{P_n} \big) \; = \; (-1)^{i-1} \mathcal{Q}\Big(\big(\otimes_{n=1}^{i-1} \chi_{P_n} \big) \otimes \big(\otimes_{n=i+1}^{N} \chi_{P_n} \big) \Big) \; \in \; \mathbb{B}_{N-1},$$

so that a_{P_i} "annihilates" the basis function χ_{P_i} and adds a corresponding sign.

(iv) *Using the anticommutator $[A, B]_+ = AB + BA$, there hold the* anticommutator relations

$$[a_f, a_g]_+ = 0, \qquad [a_f^\dagger, a_g^\dagger]_+ = 0,$$

and if $f, g \in L^2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$ are orthogonal,

$$[a_f, a_g^\dagger]_+ = [a_f^\dagger, a_g]_+ = 0.$$

If B is an orthogonal one-electron basis,

$$[a_P, a_Q^\dagger]_+ = [a_P^\dagger, a_Q]_+ = \delta_{P,Q}$$

for all $P, Q \in \mathcal{I}$, where $\delta_{P,Q} = 1$ only if $P = Q$ and $\delta_{P,Q} = 0$ otherwise. Furthermore, all creation and annihilation operators are nilpotent,

$$a_f a_f = a_f^\dagger a_f^\dagger = 0. \tag{2.13}$$

Excitation operators and excitation ranks. The annihilation and creation operoators are in particular the building blocks of excitation operators, which themselves contitute the cluster operators used in quantum chemistry: For any selection

$$I_1 < \ldots < I_r \in \text{occ}, \qquad A_1 < \ldots < A_r \in \text{virt}$$

of indices, $r \leq N$, we define a corresponding *excitation operator*

$$X_{I_1,\ldots,I_r}^{A_1,\ldots,A_r} = a_{A_1}^\dagger \ldots a_{A_r}^\dagger a_{I_1} \ldots a_{I_r}. \tag{2.14}$$

$X_{I_1,\ldots,I_r}^{A_1,\ldots,A_r}$ maps the reference determinant $\Psi_0 \in \mathbb{B}$ to a Slater determinant $\Psi_\mu \in \mathbb{B}_k$ by replacing the occupied orbitals $I_1, \ldots, I_r$ contained in Φ_0 by the virtual orbitals $A_1, \ldots, A_r$.

Thus, we have a one-to-one correspondence between the basis functions $\Psi_\mu, \mu \in \mathcal{M}^*$, and the excitation operators $X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r}$. Because both notations will be convenient in some situations, we will identify the index sets and therefore write

$$\Psi_\mu = \Psi^{A_1,\ldots,A_r}_{I_1,\ldots,I_r} := X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r}\Psi_0;$$

also, we will sometimes denote the excitation operator taking Ψ_0 to Ψ_μ by X_μ.

Note also that by Lemma 2.4,$(X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r})^\dagger = a^\dagger_{I_1}\ldots a^\dagger_{I_r}a_{A_1}\ldots a_{A_r}$, so that

$$(X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r})^\dagger\ X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r}\ \Psi_0 \ = \ (X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r})^\dagger\ \Psi^{A_1,\ldots,A_r}_{I_1,\ldots,I_r} \ = \ \Psi_0, \tag{2.15}$$

and the adjoints of excitation operators are therefore sometimes termed decitation operators.

The number $r = r(X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r}) \leq N$ of annihilators (resp. creators) contained in $X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r}$ is called the *(excitation) rank* of $X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r}$; further, we will call $\Psi_\mu = \Psi^{A_1,\ldots,A_r}_{I_1,\ldots,I_r}$ an $r-$fold excited determinant or determinant of excitation rank r, and $r(\mu) := r(X_\mu)$ the excitation rank of the index μ.
For two determinants Ψ, Ψ_s of excitation ranks $r(\mu) \neq r(\nu)$, we note that due to (2.5)

$$\langle\Psi_\mu, \Psi_\nu\rangle = \langle\Psi_\mu, \Psi_\nu\rangle_F = 0. \tag{2.16}$$

We introduce some conventions which will be useful in the following.

Definition 2.5.

(i) *For $\mu_0 := (I_1, \ldots, I_N)$ the index belonging to the reference determinant and the multiindex set $\mathcal{M}$ indexing $\mathbb{B}$, we define $\mathcal{M}^* = \mathcal{M}\backslash\{\mu_0\}$.*

(ii) *Iff $P \in \{I_1, \ldots, I_r, A_1, \ldots, A_r\}$ we say that P is contained in μ, $P \in \mu$ in short. For μ_0, we define that $P \notin \mu_0$ for all $P \in \mathcal{I}$.*

(iii) *For two multi-indices $\nu, \mu \in \mathcal{M}$, we write $\mu \subseteq \nu$ iff for all indices $P \in \mathcal{I}$, $P \in \mu$ implies $P \in \nu$.*

(iv) *Obviously, for each pair $\mu \subseteq \nu \in \mathcal{M}$, there is exactly one multi-index $\alpha \subseteq \nu \in \mathcal{M}$ determined by the condition that $P \in \alpha$ iff $P \in \nu, P \notin \mu$, and we will denote the relation between these indices by $\nu = \mu \oplus \alpha$, $\alpha = \nu \ominus \mu$.*
Additionally, we define for the situations where $\oplus, \ominus$ is not defined by the above that $\mu \oplus \alpha = -1$ if $\{P|P \in \mu\} \cap \{P|P \in \alpha\} \neq \emptyset$, and $\nu \ominus \mu = -1$ for the case $\mu \not\subseteq \nu$.

(v) *Finally, we declare for convenience that* $X_{\mu_0} = I$*, define that for coefficients turning up in summations etc.* $c_{-1}, t_{-1}, \ldots = 0$*, and also let* $\Psi_{-1} = 0, X_{-1} = 0$.

It follows from the anticommutator relations 2.4(iv) that all operators contained in any excitation operators anticommute. Therefore, $X_{\alpha\oplus\beta}$ also defines an excitation operator and there holds the important commutation relation

$$X_\alpha X_\beta \;=\; X_{\alpha\oplus\beta} \;=\; X_{\beta\oplus\alpha} \;=\; X_\beta X_\alpha$$

for any excitation operators. An analogous statement holds for products of decitation operators $X_\alpha^\dagger X_\beta^\dagger = X_{\alpha\oplus\beta}^\dagger$. Also,

$$X_\alpha^\dagger X_\beta = X_{\beta\ominus\alpha},\; X_\alpha \Psi_\beta = \Psi_{\beta\oplus\alpha},\; X_\alpha^\dagger \Psi_\beta = \Psi_{\beta\ominus\alpha}. \tag{2.17}$$

3. Cluster operators and their continuity properties

Every intermediately normed function $\Psi = \Psi_0 + \Psi^* \in \mathbb{L}^2$ can be expanded in the tensor basis $\mathbb{B}$ as

$$\Psi \;\;=\;\; \Psi_0 + \Psi^* \;=\; \Psi_0 + \sum_{\mu\in\mathcal{M}^*} t_\mu X_\mu \Psi_0 \;=:\; (I + T_{\Psi^*})\Psi_0 \tag{3.1}$$

of at most N-fold excitations $X_\mu\Psi_0$ of the reference determinant $\Psi_0 \in \mathbb{B}$. The operator T_{Ψ^*} introduced in the above is called the *cluster operator* of $\Psi \in \mathbb{L}^2$.

In the finite dimensional setting, cluster operators are automaticly continuous, implying that cluster mapping $t \mapsto e^{T(t)}$ is well-defined and continuous. From this property, according properties of the CC function can then be derived, cf. [50]. Because the Hamiltonian $\widehat{H}$ maps $\mathbb{H}^1 \to \mathbb{H}^{-1}$, the continuous formulation of the Coupled Cluster depends on according continuity properties of the infinite dimensional cluster operator and its adjoint. The following theorem formulates this result, which is fundamental for the continuous formulation of the Coupled Cluster equations. We will afterwards comment on the difficulties that have to be overcome in the proof, and then prove Theorem 3.1.

Theorem 3.1. *($\mathbb{L}^2$-/$\mathbb{H}^1$-continuity of the cluster operator and its adjoint)*

For any $\Psi^* = \sum_{\alpha\in\mathcal{M}^*} t_\alpha \Psi_\alpha$*, the cluster operator* $T = T_{\Psi^*}$ *and its* $\mathbb{L}^2$*-adjoint* $T^\dagger = T_{\Psi^*}^\dagger$ *map* $\mathbb{L}^2 \to \mathbb{L}^2$ *boundedly; there holds*

$$\|T\|_{\mathbb{L}^2\to\mathbb{L}^2} \;=\; \|T^\dagger\|_{\mathbb{L}^2\to\mathbb{L}^2} \;\sim\; \|\Psi^*\|_{\mathbb{L}^2}. \tag{3.2}$$

If $\Psi^* \in \mathbb{H}^1$, T *and* $T^\dagger$ *also map* $\mathbb{H}^1 \to \mathbb{H}^1$ *boundedly, and*

$$\|T\|_{\mathbb{H}^1 \to \mathbb{H}^1} \sim \|\Psi^*\|_{\mathbb{H}^1}, \qquad \|T^\dagger\|_{\mathbb{H}^1 \to \mathbb{H}^1} \leq \|\Psi^*\|_{\mathbb{H}^1}. \tag{3.3}$$

Using the below Lemma 3.2, the proof for (3.2) is essentially identical to the proof for the discrete ("projected") setting analysed in [50]. In contrast to this, and although the relation (3.1) between a function Ψ and its cluster operator is bluntly simple, the the $\mathbb{H}^1$-continuity (3.3) of T and $T^\dagger$ is considerably harder to verify: The operator T is easily seen to be non-compact in general, and to the authors knowledge, there are no investigations of the analytical properties of cluster operators available in the literature, except for the finite-dimensional case of CC analyzed in [50]. A direct transfer of the approaches taken there fails due to various technical obstacles arising in the continuous case: The operator $F : H^1(\mathbb{R}^3) \to H^{-1}(\mathbb{R}^3)$ fulfilling (2.5), for instance the Fock operator of the system, does not have to admit a complete eigensystem anymore; also, it was used in [50] that the discretized Hamiltonian boundedly maps to ℓ_2 for each Galerkin discretisation, so that for analysis of the *discrete* Coupled Cluster equations, the need to show the continuity of the adjoint $T^\dagger$ as mapping $\mathbb{H}^1 \to \mathbb{H}^1$ could be avoided. This is not the case any more in the continuous setting. Note also that the continuity of $T : \mathbb{H}^1 \to \mathbb{H}^1$ only implies the continuity of its $\mathbb{H}^1$-adjoint $T^{\dagger,\mathbb{H}^1} : \mathbb{H}^{-1} \to \mathbb{H}^{-1}$, but not the $\mathbb{H}^1$-continuity of the restriction of the $\mathbb{L}_2$-adjoint $T^\dagger : \mathbb{L}_2 \to \mathbb{L}_2$ to $\mathbb{H}^1$.

Our proof given here starts by showing that we can without loss of generality suppose that the spin basis B that determines Ψ^* and T is $\mathbb{L}_2$-orthonormal in Lemma 3.2. We will then provide an expression for the $\mathbb{H}^1$-equivalent F-norm of functions as induced by the operator F^N from (2.9), Lemma 3.4. To show that images of T and $T^\dagger$ are bounded in this norm, we then prove an appropriate extension of an estimate from [50], based on the nilpotency property of annihilation and creation operators in Lemma 3.5; this estimate will then apply to prove the $\mathbb{H}^1$-continuity of the operators T and $T^\dagger$.

Lemma 3.2. *(Reduction to orthonormal basis sets)*

Let $\tilde{B} := \{\tilde{\chi}_I \mid I \in occ\} \cup \{\tilde{\chi}_A \mid A \in virt\}$ *be an* L_2*-orthonormal basis for which there holds*

$$\mathrm{span}\{\tilde{\chi}_I | I \in occ\} = \mathrm{span}\{\chi_I | I \in occ\}, \qquad \mathrm{span}\{\tilde{\chi}_A | A \in virt\} = \mathrm{span}\{\chi_A | A \in virt\},$$

and denote by $\tilde{\Psi}_\alpha$ *the elements of the tensor basis constructed from* $\tilde{B}$ *and by* $\tilde{X}_\alpha, \alpha \in \mathcal{M}^*$, *the excitation operators constructed from the creators and annihilators belonging to the basis functions from* $\tilde{B}$.

(i) *There holds* $\mathrm{span}\{\Psi_\alpha | \alpha \in \mathcal{M}^*\} = \mathrm{span}\{\tilde{\Psi}_\alpha | \alpha \in \mathcal{M}^*\}$.

(ii) *For the cluster operator* $T = \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha$ *belonging to*

$$\Psi^* \;=\; \sum_{\alpha \in \mathcal{M}^*} t_\alpha \Psi_\alpha \;=\; \sum_{\alpha \in \mathcal{M}^*} \tilde{t}_\alpha \tilde{\Psi}_\alpha \;\in\; \mathrm{span}\{\Psi_\alpha | \alpha \in \mathcal{M}^*\},$$

there also holds $T = \sum_{\alpha \in \mathcal{M}^*} \tilde{t}_\alpha \tilde{X}_\alpha$.

Proof. First of all, (2.16) gives that $\langle \Psi_0, \Psi_\alpha \rangle = 0$ and (2.5) implies that $\langle \tilde{\Psi}_0, \Psi_\alpha \rangle = 0$ for all $\alpha \in \mathcal{M}^*$, implying $\mathrm{span}\{\Phi_0\} = \mathrm{span}\{\tilde{\Phi}_0\}$ and thus, with (2.16), $\mathrm{span}\{\Psi_\alpha | \alpha \in \mathcal{M}^*\} = \mathrm{span}\{\tilde{\Psi}_\alpha | \alpha \in \mathcal{M}^*\}$. Let us denote by $\tilde{a}_P, \tilde{a}_P^\dagger$ the annihilator/creator of $\tilde{\chi}_P$, respectively. Again using (2.5), we can expand

$$\chi_I = \sum_{J \in \mathrm{occ}} c_I^J \tilde{\chi}_J, \quad \chi_A = \sum_{B \in \mathrm{virt}} c_A^B \tilde{\chi}_B, \quad a_I = \sum_{J \in \mathrm{occ}} c_I^J \tilde{a}_J, \quad a_A^\dagger = \sum_{B \in \mathrm{virt}} c_A^B \tilde{a}_B^\dagger,$$

where we inserted the expansions for χ_I, χ_A into the representations (2.10) and (2.12) for the creation and annihilation operators. Thus, for suitable coefficients $d_\alpha^{\alpha'}$, $\alpha, \alpha' \in \mathcal{M}^*$,

$$T = \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha = \sum_{\alpha \in \mathcal{M}^*} t_\alpha \Big(\sum_{\substack{\alpha' \in \mathcal{M}^* \\ \mathrm{rk}(\alpha') = \mathrm{rk}(\alpha)}} d_\alpha^{\alpha'} \Big) \tilde{X}_\alpha = \sum_{\alpha' \in \mathcal{M}^*} \Big(\sum_{\substack{\alpha \in \mathcal{M}^* \\ \mathrm{rk}(\alpha') = \mathrm{rk}(\alpha)}} t_\alpha d_\alpha^{\alpha'} \Big) \tilde{X}_{\alpha'}. \tag{3.4}$$

Because

$$\sum_{\alpha \in \mathcal{M}^*} \tilde{t}_\alpha \tilde{X}_\alpha \Psi_0 = \Psi^* = T \Psi_0 = \sum_{\alpha' \in \mathcal{M}^*} \Big(\sum_{\substack{\alpha \in \mathcal{M}^* \\ \mathrm{rk}(\alpha') = \mathrm{rk}(\alpha)}} t_\alpha d_\alpha^{\alpha'} \Big) \tilde{X}_{\alpha'} \Psi_0,$$

the coefficients to the very left and the very right coincide, so (ii) follows from (3.4).

□

We will now of course use Lemma 3.2 and assume that B is orthonormal. To prove the continuity of $T : \mathbb{H}^1 \to \mathbb{H}^1$, we now equip $\mathbb{H}^1$ with the equivalent norm induced by the mapping F^N, see Assumption 2.1. We will then expand $T\Psi$ in suitable orthonormal bases (Lemma 3.4) and estimate the occurring terms by the below Lemma 3.5. We start by introducing some short-hand notations for occurring terms.

Notations 3.3. *(Notations used in the proof of Theorem 3.1)*

(i) *By standard Hilbert space theory, we can choose an* F*-orthonormal one-particle basis*

$$\overline{B} := \{\overline{\chi}_P | \; P \in \mathcal{I}\} \tag{3.5}$$

for which

$$span\{\overline{\chi}_I|\ I \in occ\} = span\{\chi_I|\ I \in occ\}.$$

(ii) *The index* $\mu \in \mathcal{M}^*$ *belonging to a onefold excitation operators* $X_I^A, I \in occ, A \in virt$, *will be denoted as* $\mu = \binom{I}{A}$.

(iii) *For an index* $I \in occ$, *let* $|I|$ *label its position* $p \in \{1, \ldots, N\}$ *in the reference determinant (2.6), and denote* $\sigma_I := (-1)^{|I|}$.

(iv) *For* $\mu \in \mathcal{M}$, *we denote*

$$\rho_\mu := \frac{1}{r(\mu) - 1}. \tag{3.6}$$

(v) *Finally, for each* $\mu \in \mathcal{M}$, *we define a corresponding mapping* $\mu : occ \to \mathcal{I}$: *If* $I \notin \mu$ *(i.e. if the occupied orbital* χ_I *is "not excited by* X_μ*"), we let* $\mu(I) = I$; *if* $I \in \mu$, *we have in equation (2.14) that* $I = I_s$ *for some* $s \in \{1, \ldots, r\}$, *and* I_s *defines by the ordering on* $\mathcal{I}$ *a unique virtual index* A_s *(to which the orbital* χ_I *is "excited by* X_μ*"), for which we then define* $\mu(I) = A_s$.

The following lemma provides a working expression for the F-norm of a wave function Ψ.

Lemma 3.4. *(F-norm of antisymmetric functions)*

For any $\Psi = \sum_{\mu \in \mathcal{M}} d_\mu \Psi_\mu \in \mathbb{H}^1$, *there holds*

$$\begin{aligned} \|\Psi\|_F^2 = & \sum_{J \in occ} \sum_{\nu \in \mathcal{M}} \Big| \sum_{\substack{I \in occ \\ I \notin \nu}} \sigma_I\ d_\nu\ \langle \chi_I, \overline{\chi}_J \rangle_F \Big|^2 \\ & + \sum_{B \in virt} \sum_{\nu \in \mathcal{M}} \rho_\nu \Big| \sum_{I \in occ} \sum_{A \in virt} \sigma_I d_{\nu \oplus \binom{A}{I}} \langle \chi_A, \overline{\chi}_B \rangle_F \Big|^2. \end{aligned} \tag{3.7}$$

Proof. We will show that for any $i \in \{1, \ldots, N\}$, there holds

$$\|\Psi\|_{F_i}^2 = \frac{1}{N} \Big(\sum_{\substack{J \in \mathrm{occ} \\ \nu \in \mathcal{M}}} \Big| \sum_{\substack{I \in \mathrm{occ} \\ I \notin \nu}} \sigma_I\ d_\nu\ \langle \chi_I, \overline{\chi}_J \rangle_F \Big|^2 + \sum_{\substack{B \in \mathrm{virt} \\ \nu \in \mathcal{M}}} \rho_\nu \Big| \sum_{\substack{I \in \mathrm{occ} \\ A \in \mathrm{virt}}} \sigma_I d_{\nu \oplus \binom{A}{I}} \langle \chi_A, \overline{\chi}_B \rangle_F \Big|^2 \Big). \tag{3.8}$$

By definition of $F = F_N$, we have $\|\Psi\|_F^2 = \sum_{i=1}^N \|\Psi\|_{F_i}^2$ for any $\Psi \in \mathbb{H}^1$, and the lemma is then proven. To make notations not more complicated than necessary, we suppose $i = 1$ without loss of generality. We define an orthonormal basis with respect to the F_1-inner product: Let us denote by $\overline{\mathcal{M}} \subseteq I^{N-1}$ the set of ordered indices of length $N - 1$, and

denote for $\overline{\nu} \in \overline{\mathcal{M}}$ by $\Phi_{\overline{\nu}}$ the $(N-1)$-electron Slater determinant formed from the one-particle basis functions from B as determined by $\overline{\nu}$. Using $\overline{\chi}_P$ as defined in (3.5), the set

$$\overline{\mathbb{B}} \;:=\; \{\Psi_{P\overline{\nu}} := \overline{\chi}_P \otimes \Phi_{\overline{\nu}} \mid P \in \mathcal{J}, \overline{\nu} \in \overline{\mathcal{M}}\}$$

is an F_1-orthonormal system. We can write every basis function $\Psi_\mu \in \mathbb{B}$ as

$$\Psi_\mu \;=\; \frac{1}{N!} \sum_{\pi \in S(N)} (-1)^{|\pi|}\, \chi_{\mu_{\pi(1)}} \otimes \ldots \otimes \chi_{\mu_{\pi(N)}} \;=\; \frac{1}{N} \sum_{I \in \mathrm{occ}} \sigma_I\, \chi_{\mu(I)} \otimes \Phi_{\overline{\mu}_I}, \tag{3.9}$$

where $\Phi_{\overline{\mu}_I}$ is the Slater determinant from $\overline{\mathbb{B}}$ obtained from Ψ_μ by removing the function $\chi_{\mu(I)}$. Therefore, $\mathbb{H}^1$ is contained in the F_1-span of $\overline{\mathbb{B}}$, and we can calculate the F_1-norm of any $\Psi \in \mathbb{H}^1$ by expanding Ψ in the basis $\overline{\mathbb{B}}$. To do so, we decompose for fixed $I \in \mathrm{occ}$ the set $\mathcal{M}$ into indices belonging to excitation operators that do not/do contain the annihilator for I,

$$\sum_{\mu \in \mathcal{M}} d_\mu\, (\chi_{\mu(I)} \otimes \Phi_{\overline{\mu}_I}) \;=\; \sum_{\substack{\mu \in \mathcal{M} \\ I \notin \mu}} d_\mu\, (\chi_I \otimes \Phi_{\overline{\mu}_I}) \;+\; \sum_{\substack{\mu \in \mathcal{M} \\ I \notin \mu}} \rho_\mu \sum_{A \in \mathrm{virt}} d_{\mu \oplus \binom{A}{I}}\, (\chi_A \otimes \Phi_{\overline{\mu}_I}).$$

Note that in the second term, there are $r(\mu)+1$ combinations of indices $\mu, \binom{A}{I}$ that give rise to the same summand indexed by $\mu \oplus \binom{A}{I}$, causing the factor ρ_μ. Inserting (3.9) into $\Psi = \sum_{\mu \in \mathcal{M}} d_\mu \Psi_\mu$, interchanging sums and then using the above decomposition gives

$$\Psi = \frac{1}{N} \sum_{I \in \mathrm{occ}} \sigma_I \sum_{\substack{\mu \in \mathcal{M} \\ I \notin \mu}} \Big(d_\mu\, (\chi_{\mu(I)} \otimes \Phi_{\overline{\mu}_I}) + \rho_\mu \sum_{A \in \mathrm{virt}} d_{\mu \oplus \binom{A}{I}}\, (\chi_A \otimes \Phi_{\overline{\mu}_I}) \Big). \tag{3.10}$$

Let $I \in \mathrm{occ}$ and $\overline{\nu} = (I_{\overline{\nu}_1}, \ldots, I_{\overline{\nu}_m}, A_{\overline{\nu}_1}, \ldots, A_{\overline{\nu}_{N-1-m}}) \in \overline{\mathcal{M}}$ be fixed. Then $\overline{\nu}$ defines a unique excitation operator $\nu_I \in \mathcal{M}$ by defining $\mathrm{occ}(\nu_I) = \mathrm{occ} \backslash \{I, I_{\overline{\nu}_1}, \ldots, I_{\overline{\nu}_m}\}$, $\mathrm{virt}(\nu_I) = \{A_{\overline{\nu}_1}, \ldots, A_{\overline{\nu}_{N-1-m}}\}$. The relation $(\overline{\nu}, \nu_I)$ defines a bijection between the set $\overline{\mathcal{M}}$ and the set$\{\mu \in \mathcal{M} | I \notin \mu\}$. If we let $\delta^I_{\overline{\nu},\mu} = 1$ if $\nu_I = \mu$ and zero elsewise, testing (3.10) with $\Psi_{P\overline{\nu}}$ yields

$$\langle \Psi, \Psi_{P\overline{\nu}} \rangle = \frac{1}{N} \sum_{I \in \mathrm{occ}} \sigma_I \sum_{\substack{\mu \in \mathcal{M} \\ I \notin \mu}} \Big(d_\mu\, \langle \chi_I, \overline{\chi}_P \rangle_F\, \delta^I_{\overline{\nu},\mu} + \rho_\mu \sum_{A \in \mathrm{virt}} d_{\mu \oplus \binom{I}{A}}\, \langle \chi_A, \overline{\chi}_P \rangle_F \delta^I_{\overline{\nu},\mu} \Big).$$

Therefore, we get

$$\begin{aligned}\|\Psi\|_{F_1}^2 &= \frac{1}{N}\sum_{P\in\mathcal{J}}\sum_{\overline{\nu}\in\overline{\mathcal{M}}}\Big|\sum_{I\in\mathrm{occ}}\sigma_I\sum_{\substack{\mu\in\mathcal{M}\\ I\notin\mu}}\Big(d_\mu\ \langle\chi_I,\overline{\chi}_P\rangle_F\ \delta^I_{\overline{\nu},\mu}+\rho_\mu\sum_{A\in\mathrm{virt}}d_{\mu\oplus\binom{I}{A}}\ \langle\chi_A,\overline{\chi}_P\rangle_F\delta^I_{\overline{\nu},\mu}\Big)\Big|^2\\ &= \frac{1}{N}\sum_{P\in\mathcal{J}}\sum_{\nu\in\mathcal{M}}\Big|\sum_{\substack{I\in\mathrm{occ}\\ I\notin\nu}}\sigma_I\Big(\ d_\mu\langle\chi_I,\overline{\chi}_P\rangle_F\ +\ \rho_\mu\sum_{A\in\mathrm{virt}}d_{\mu\oplus\binom{I}{A}}\langle\chi_A,\overline{\chi}_P\rangle_F\ \Big)\Big|^2.\end{aligned}$$

Using that $d_{\mu\oplus\binom{I}{A}}=0$ if $I\in\nu$ and the orthogonality condition (2.5), one obtains the desired expression (3.8), implying (3.7).

□

The first estimate in next lemma was already proven in [50], where it was central to the analysis for the projected CC equations the discrete setting. We re-formulate it here with an improved constant and derive from it the estimate (3.12), which will be useful to show continuity of $T^\dagger$.

Lemma 3.5. *(Estimate for the proof of Theorem 3.1)*

For any sequences $(d_\beta)_{\beta\in\mathcal{M}},(e_\beta)_{\beta\in\mathcal{M}}\in\ell_2(\mathcal{M})$, there holds

$$\sum_{\nu\in\mathcal{M}}\Big|\sum_{\beta\in\mathcal{M}}d_\beta e_{\nu\ominus\beta}\Big|^2\ \le\ C_N\ \|(d_\beta)_{\beta\in\mathcal{M}}\|^2_{\ell_2(\mathcal{M})}\ \|(e_\beta)_{\beta\in\mathcal{M}}\|^2_{\ell_2(\mathcal{M})} \tag{3.11}$$

and also

$$\sum_{\nu\in\mathcal{M}}\Big|\sum_{\beta\in\mathcal{M}}d_\beta e_{\nu\oplus\beta}\Big|^2\ \le\ C_N\ \|(d_\beta)_{\beta\in\mathcal{M}}\|^2_{\ell_2(\mathcal{M})}\ \|(e_\beta)_{\beta\in\mathcal{M}}\|^2_{\ell_2(\mathcal{M})}. \tag{3.12}$$

Proof. We start by estimating the number of indices μ for which $\mu\subseteq\nu$ holds for a fixed index ν (and thus for the number of indices μ for which $\nu\ominus\mu$ gives a nonzero contribution): By definition, $\mu\subseteq\nu$ iff $\mathrm{virt}(\mu)\subseteq\mathrm{virt}\ (\nu)$ and $\mathrm{occ}(\nu)\subseteq\mathrm{occ}\ (\mu)$, so the number of possible indices $\mu\subseteq\nu$ for which Φ_μ has excitation rank s is given by $\binom{r}{s}\binom{N}{(N-s)-(N-r)}=\binom{r}{s}\binom{N}{r-s}$, where r denotes the excitation rank of Φ_ν. Summing up over all ranks $s\le r$ gives

$$\sum_{0\le s\le r}\binom{r}{s}\binom{N}{r-s}\ =\ \binom{N+r}{r}\ \le\ \binom{2N}{N}\ =:\ C_N$$

by Vandermonde's identity and a (sharp) worst-case estimate. Now, we can estimate the left hand of (3.11) by noting that for every fixed ν, the sum over β contains at most C_N

non-null summands; thus

$$\sum_{\nu\in\mathcal{M}} \Big| \sum_{\beta\in\mathcal{M}} d_\beta e_{\nu\ominus\beta}\Big|^2 \;\le\; C_N \sum_{\nu\in\mathcal{M}}\sum_{\beta\in M} \big|d_\beta\big|^2 \big|e_{\nu\ominus\beta}\big|^2 \;\le\; C_N \sum_{\beta\in\mathcal{M}} \big|d_\beta\big|^2 \sum_{\nu\in\mathcal{M}} \big|e_\nu\big|^2,$$

giving (3.11).
To prove (3.12), we note that (3.11) means that for $(d_\beta)_{\beta\in\mathcal{M}} \in \ell_2(\mathcal{M})$, the mapping

$$M : (f_\delta)_{\delta\in\mathcal{M}} \mapsto \big(\sum_{\nu\in\mathcal{M}} f_\nu d_{\delta\ominus\nu}\big)_{\delta\in\mathcal{M}}$$

is a continuous mapping $\ell_2(\mathcal{M}) \to \ell_2(\mathcal{M})$ with continuity constant $\|M\| \le C_N^{\frac{1}{2}} \|d_\beta\|_{\ell_2}$.
We compute the adjoint of M: Because there holds for $(e_\delta)_\delta \in \ell_2(\mathcal{M})$ that

$$\big\langle M(f_\delta)_{\delta\in\mathcal{M}}, (e_\delta)_{\delta\in\mathcal{M}}\big\rangle \;\;=\;\; \sum_{\delta\in\mathcal{M}}\sum_{\nu\in\mathcal{M}} f_\nu d_{\delta\ominus\nu} e_\delta \;=\; \big\langle (f_\nu)_{\nu\in\mathcal{M}}, (\sum_{\delta\in\mathcal{M}} d_{\delta\ominus\nu} e_\delta)_{\nu\in\mathcal{M}}\big\rangle$$

and for fixed $\nu \in \mathcal{M}$ that

$$\sum_{\delta\in\mathcal{M}} d_{\delta\ominus\nu} e_\delta \;=\; \sum_{\nu\subseteq\delta\in\mathcal{M}} d_{\delta\ominus\nu} e_\delta \;=\; \sum_{\beta\in\mathcal{M}} d_\beta e_{\nu\oplus\beta},$$

$M^\dagger$ is given by

$$M^\dagger :\; (e_\beta)_{\beta\in\mathcal{M}} \;\mapsto\; \big(\sum_{\beta\in\mathcal{M}} d_\beta e_{\nu\oplus\beta}\big)_{\nu\in\mathcal{M}}.$$

$M^\dagger$ is also continuous with $\|M^\dagger\| = \|M\| \le C_N^{\frac{1}{2}} \|(d_\beta)_{\beta\in\mathcal{M}}\|_{\ell_2}$, and writing this out gives (3.12).

□

Proof of Theorem 3.1: Using the estimate (3.11), the proof of the $\mathbb{L}^2$-continuity of T is completely analogous to the proof of [50], Lemma 4.13, for the discrete case. We therefore leave it out for sake of brevity. To show that T continuously maps $\mathbb{H}^1 \to \mathbb{H}^1$, we denote

$$\Psi = \sum_{\mu\in\mathcal{M}} c_\mu \Psi_\mu,\;\; \Psi^* = \sum_{\alpha\in\mathcal{M}^*} t_\alpha \Psi_\alpha,\;\; T\Psi = \sum_{\nu\in\mathcal{M}^*} d_\nu \Psi_\nu = \sum_{\mu\in\mathcal{M}}\sum_{\alpha\in\mathcal{M}^*} t_\alpha c_\mu X_{\alpha\oplus\mu}\Psi_0.$$

We now compute the F-norm for $T\Psi$ according to Lemma 3.4: For $\nu \in \mathcal{M}, A \in \mathrm{virt}$, there holds

$$\begin{aligned} d_\nu &= \sum_{\mu\in\mathcal{M}}\sum_{\alpha\in\mathcal{M}^*} t_\alpha c_\mu \delta_{\alpha\oplus\mu,\nu} = \sum_{\alpha\in\mathcal{M}^*} t_\alpha c_{\nu\ominus\alpha}, \\ \sum_{I\in\mathrm{occ}} d_{\nu\oplus\binom{A}{I}} &= \sum_{I\in\mathrm{occ}}\sum_{\mu\in\mathcal{M}}\sum_{\alpha\in\mathcal{M}^*} \big(t_{\alpha\oplus\binom{A}{I}} c_\mu \delta_{\alpha\oplus\mu,\nu} + t_\alpha c_{\mu\oplus\binom{A}{I}}\big)\delta_{\alpha\oplus\mu,\nu} \\ &= \sum_{\substack{I\in\mathrm{occ}\\ I\notin\nu}}\sum_{\alpha\in\mathcal{M}^*} t_{\alpha\oplus\binom{A}{I}} c_{\nu\ominus\alpha} + t_{\nu\ominus\alpha} c_{\alpha\oplus\binom{A}{I}}. \end{aligned}$$

Thus, inserting this in (3.7),

$$\begin{aligned} \|T\Psi\|_F^2 &= \sum_{J\in\mathrm{occ}}\sum_{\nu\in\mathcal{M}} \Big| \sum_{\substack{I\in\mathrm{occ}\\ I\notin\nu}} \sigma_I \sum_{\alpha\in\mathcal{M}^*} t_\alpha c_{\nu\ominus\alpha} \,\langle \chi_I, \overline{\chi}_J\rangle_F\Big|^2 \qquad (3.13) \\ &+ \sum_{B\in\mathrm{virt}}\sum_{\nu\in\mathcal{M}} \rho_\nu \Big| \sum_{I\in\mathrm{occ}}\sum_{A\in\mathrm{virt}} \sigma_I \sum_{\alpha\in\mathcal{M}^*} \big(t_{\alpha\oplus\binom{A}{I}} c_{\nu\ominus\alpha} + t_{\nu\ominus\alpha} c_{\alpha\oplus\binom{A}{I}}\big)\langle \chi_A, \overline{\chi}_B\rangle_F\Big|^2. \end{aligned}$$

Denoting the summand in line (3.13) with (I) and the one in the line below with (II), we can use the estimate (3.11) to obtain for (I) that

$$\begin{aligned} \text{(I)} &\le \sum_{J\in\mathrm{occ}}\sum_{\nu\in\mathcal{M}} \Big(\sum_{\substack{I\in\mathrm{occ}\\ I\notin\nu}} \Big| \sum_{\alpha\in\mathcal{M}^*} t_\alpha c_{\nu\ominus\alpha} \,\langle \chi_I, \overline{\chi}_J\rangle_F\Big|\Big)^2 \\ &\le N\cdot \Big(\sum_{I\in\mathrm{occ}}\sum_{J\in\mathrm{occ}} \big|\langle \chi_I, \overline{\chi}_J\rangle_F\big|^2\Big) \sum_{\nu\in\mathcal{M}} \Big| \sum_{\alpha\in\mathcal{M}^*} t_\alpha c_{\nu\ominus\alpha}\Big|^2 \\ &\le NC_N\Big(\sum_{I\in\mathrm{occ}} \|\chi_I\|_F^2\Big)\ \|t_\alpha\|_{\ell_2(\mathcal{M})}^2\ \|c_\alpha\|_{\ell_2(\mathcal{M})}^2 \\ &\lesssim \|\Psi^*\|\cdot\|\Psi\|, \end{aligned}$$

while for (II),

$$\begin{aligned} \text{(II)} \le\ & 2\sum_{B\in\mathrm{virt}}\sum_{\nu\in\mathcal{M}} \rho_\nu \Big| \sum_{I\in\mathrm{occ}}\sum_{A\in\mathrm{virt}} \sigma_I \sum_{\alpha\in\mathcal{M}^*} t_{\alpha\oplus\binom{A}{I}} c_{\nu\ominus\alpha} \langle \chi_A, \overline{\chi}_B\rangle_F\Big|^2 \qquad (3.14) \\ &+ 2\sum_{B\in\mathrm{virt}}\sum_{\nu\in\mathcal{M}} \rho_\nu \Big| \sum_{I\in\mathrm{occ}}\sum_{A\in\mathrm{virt}} \sigma_I \sum_{\alpha\in\mathcal{M}^*} t_{\nu\ominus\mu} c_{\mu\oplus\binom{A}{I}} \langle \chi_A, \overline{\chi}_B\rangle_F\Big|^2. \qquad (3.15) \end{aligned}$$

To estimate the summand in line (3.14), we use that for $\alpha \subseteq \nu$, $\rho_\nu \leq \rho_\alpha$, and apply (3.11) afterwards to obtain

$$\begin{aligned}
&\sum_{B\in\mathrm{virt}}\sum_{\nu\in\mathcal{M}} \rho_\nu \Big| \sum_{I\in\mathrm{occ}}\sum_{A\in\mathrm{virt}} \sigma_I \sum_{\alpha\in\mathcal{M}^*} t_{\alpha\oplus\binom{A}{I}} c_{\nu\ominus\alpha} \langle \chi_A, \overline{\chi}_B\rangle_F \Big|^2 \\
\leq\ & \sum_{B\in\mathrm{virt}}\sum_{\nu\in\mathcal{M}} \Big| \sum_{\alpha\in\mathcal{M}^*} \Big(\rho_\alpha \sum_{I\in\mathrm{occ}}\sum_{A\in\mathrm{virt}} \sigma_I\ t_{\alpha\oplus\binom{A}{I}} \langle \chi_A, \overline{\chi}_B\rangle_F \Big) c_{\nu\ominus\alpha} \Big|^2 \\
\lesssim\ & \Big(\sum_{B\in\mathrm{virt}}\sum_{\alpha\in\mathcal{M}} \rho_\alpha \Big| \sum_{I\in\mathrm{occ}}\sum_{A\in\mathrm{virt}} \sigma_I t_{\alpha\oplus\binom{A}{I}} \langle \chi_A, \overline{\chi}_B\rangle_F \Big|^2 \Big) \cdot \|(c_\nu)_{\nu\in\mathcal{M}}\|_{\ell_2(\mathcal{M})} \\
\leq\ & \|\Psi^*\|_F \cdot \|\Psi\|
\end{aligned}$$

by comparison with the expression for the F-norm of Ψ^*, while the same proceeding with the summand in line (3.15) gives the other way around

$$2 \sum_{B\in\mathrm{virt}}\sum_{\nu\in\mathcal{M}} \rho_\nu \Big| \sum_{I\in\mathrm{occ}}\sum_{A\in\mathrm{virt}} \sigma_I \sum_{\alpha\in\mathcal{M}^*} t_{\nu\ominus\mu} c_{\mu\oplus\binom{A}{I}} \langle \chi_A, \overline{\chi}_B\rangle_F \Big|^2 \ \lesssim\ \|\Psi^*\| \cdot \|\Psi\|_F.$$

Thus altogether, $\|T\Psi\|_F \lesssim \|\Psi^*\|_F \cdot \|\Psi\|_F$, and observing $\|T\Psi_0\| = \|\Psi^*\|$ finishes the first part of the proof. It remains to show the $\mathbb{H}^1$-continuity of $T^\dagger$, for which the proof is analogous to that for T, with the estimate (3.12) entering instead of (3.11); we therefore only sketch the proceeding. Again, the representation (3.7) is used to compute $\|T^\dagger\Psi\|_F$. Denoting

$$T^\dagger\Psi \ = \ \sum_{\nu\in\mathcal{M}} d_\nu \Psi_\nu \ = \ \sum_{\alpha\in\mathcal{M}^*}\sum_{\mu\in\mathcal{M}} t_\alpha c_\mu X_{\mu\ominus\alpha}\Psi_0,$$

the coefficients d_n are this time for fixed $I \in \mathcal{I}$, $\nu \in \mathcal{M}$, $I \notin \nu$ given by

$$d_\nu = \sum_{\alpha\in\mathcal{M}^*} t_\alpha c_{\nu\oplus\alpha};\ d_{\nu\oplus\binom{A}{I}} \ = \ \sum_{\alpha\in\mathcal{M}^*} t_\alpha c_{\nu\oplus\alpha\oplus\binom{A}{I}}.$$

Inserting this in (3.7) for $\|T^\dagger\Psi\|_F$ gives two terms, which can be estimated analogously to the above, only that $\rho_{\nu\oplus\alpha} \leq (N+1)\rho_\nu$ enters instead of $\rho_\alpha \leq \rho_\nu$. We then obtain

$$\|T^\dagger\Psi\|_F \ \lesssim\ \|\Psi^*\| \cdot \|\Psi\| \ + \ \|\Psi^*\| \cdot \|\Psi\|_F \ \lesssim\ \|\Psi^*\| \cdot \|\Psi\|_F,$$

and thus the upper bound for the $\mathbb{H}^1$-norm of $T^\dagger$.

□

Note that the F-norm of Ψ^* does not enter the above estimate for $T^\dagger = T^\dagger_{\Psi^*}$. Therefore, the H^1-norm of $T^\dagger$ is not uniformly bounded from below by the H^1-norm of Ψ^* because we can choose a sequence Ψ^*_n for which $\|\Psi^*_n\|_F = 1$ but $\|\Psi^*_n\| \to 0$; there then holds

$\|T^\dagger_{\Psi^*_n}\|_F / \|\Psi^*_n\|_F \leq \|\Psi^*_n\| / \|\Psi^*\|_F \to 0.$

Corollary 3.6. *(Continuity of $T : \mathbb{H}^{-1} \to \mathbb{H}^{-1}$)*

Each cluster operator $T = T_{\Psi^*}$, $\Psi^* \in \mathbb{H}^1$, can be extended to a continuous operator $T : \mathbb{H}^{-1} \to \mathbb{H}^{-1}$. In particular, each excitation operator X_μ can be continuously extended to an operator $\mathbb{H}^{-1} \to \mathbb{H}^{-1}$, and there holds $T = \sum_{\mu \in \mathcal{M}^*} c_\mu X_\mu$ in $\mathbb{H}^{-1}$.

Proof. Because $T^\dagger$ is bounded on $\mathbb{H}^1$, its adjoint $\tilde{T} : \mathbb{H}^{-1} \to \mathbb{H}^{-1}$ is also continuous with $\|\tilde{T}\|_{\mathbb{H}^{-1} \to \mathbb{H}^{-1}} = \|T^\dagger\|_{\mathbb{H}^1 \to \mathbb{H}^1}$, and for every $F(\cdot) \in (\mathbb{L}^2)' \subseteq \mathbb{H}^{-1}$ (which we can write as $\langle \Psi, \cdot \rangle$ with $\Psi \in \mathbb{L}^2$), there holds

$$\tilde{T}F \;:=\; F(T^\dagger \cdot) \;=\; \langle \Psi, T^\dagger \cdot \rangle \;=\; \langle T\Psi, \cdot \rangle,$$

so that $\tilde{T}$ defines a continuous extension of T (which we also denoted as T above). Theorem 3.1 in particular implies that $X_\mu : \mathbb{H}^{-1} \to \mathbb{H}^{-1}$ is continuous and well-defined, and T and $\sum_{\mu \in \mathcal{M}^*} c_\mu X_\mu$ coincide on the dense subset $\mathbb{L}^2$, so $T = \sum_{\mu \in \mathcal{M}^*} c_\mu X_\mu$ also follows. □

4. The continuous Coupled Cluster equations

We now define the continuous version of the Coupled Cluster equations as the main result, Theorem 4.4. The eigenvalue equation (1.1) can be rewritten in terms of the cluster operator T as the problem of finding a coefficient vector $t^* = (t_\alpha)_{\alpha \in \ell_2(\mathcal{M})} \in \ell_2(\mathcal{M}^*)$ such that for $T = \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha$ there holds $\Psi^* := T\Psi_0 \in \mathbb{H}^1$ and

$$\langle \Psi_\mu,\; (H - E^*)\,(I + T)\Psi_0 \rangle \;=\; 0 \text{ for all } \Psi_\mu \;\in\; \mathbb{B}.$$

The solution of (1.1) is then given by $\Psi = \Psi_0 + \Psi^*$. Note that in the above, only coefficient vectors $t^* = (t_\alpha)_{\alpha \in \mathcal{M}^*}$ are admitted for which the corresponding function Ψ^* is contained in $\mathbb{H}^1$. This is reflected by restricing the set of admissible coefficients from $\ell_2(\mathcal{M}^*)$ in the following way.

Definition 4.1. *(The H^1-coefficient space $\mathbb{V}$)*

Let $\langle \cdot, \cdot \rangle_{\hat{F}} : (\mathrm{span}\{\Psi_0\})^\perp \times (\mathrm{span}\{\Psi_0\})^\perp \to \mathbb{R}$ denote an inner product which on $(\mathrm{span}\{\Psi_0\})^\perp$ induces a norm equivalent to the $\mathbb{H}^1$-norm. We define a subspace $\mathbb{V} \subseteq \ell_2(\mathcal{M}^*)$ by

$$\mathbb{V} \;:=\; \{ t \in \ell_2(\mathcal{M}^*) \mid \|t\|_{\mathbb{V}} < \infty \}.$$

where

$$\langle t, s\rangle_{\mathbb{V}} \;:=\; \langle \sum_{\alpha\in\mathcal{M}^*} t_\alpha \Psi_\alpha, \sum_{\beta\in\mathcal{M}^*} s_\beta \Psi_\beta\rangle^2_{\hat{F}}, \qquad \|t\|_{\mathbb{V}} \;:=\; \langle t, t\rangle^{1/2}_{\mathbb{V}}. \tag{4.1}$$

□

The above definition of $\mathbb{V}$ is independent of the particular choice of the norm $\|\cdot\|_{\hat{F}}$. Denoting as $T(t)$ the cluster operator defined by t and $\Psi(t) := T(t)\Psi_0$, there holds

$$\|t\|_{\mathbb{V}} \;\sim\; \|\Psi(t)\|_{\mathbb{H}^1}; \tag{4.2}$$

in particular, $t \in \mathbb{V}$ iff $\Psi^*(t) \in \mathbb{H}^1 \cap (\mathrm{span}\{\Psi_0\})^\perp$, so $(\mathbb{V}, \langle\cdot,\cdot\rangle_{\mathbb{V}})$ is complete and thus is a Hilbert space. For practical purposes, the Fock or Kohn-Sham operator F, shifted by the sum Λ_0 of the N eigenvalues belonging to the subspace spanned by the occupied orbitals, can be used if F fulfils a spinwise HOMO-LUMO condition: $\hat{F} = F - \Lambda_0 I$ is then positive definite on on $(\mathrm{span}\{\Psi_0\})^\perp$, see [46] for the proof. Also note that although this mapping is particularly convenient to handle if B is an eigenbasis of the operator F, so that F is diagonal in this basis, evaluation of F in a non-orthogonal, non-eigenbasis may also be performed within reasonable complexity if F is a one-particle operator like F_{HF} or F_{KS}.
The continuity properties of the cluster operators imply continuity of the linear mappings relating a vector $t \in \mathbb{V}$ with an according cluster operator:

Corollary 4.2. *The linear mappings*

$$t \;\mapsto\; T(t) = \sum_{\alpha\in\mathcal{M}^*} t_\alpha X_\alpha, \qquad\qquad t \;\mapsto\; T^\dagger(t) = \sum_{\alpha\in\mathcal{M}^*} t_\alpha X^\dagger_\alpha$$

are bounded linear mappings $(\mathbb{V}, \|\cdot\|_{\mathbb{V}}) \;\to\; (B(\mathbb{H}^1), \|\cdot\|_{\mathbb{H}^1\to\mathbb{H}^1})$.

To formulate the CC equations, we need one more lemma justifying the exponential parametrisation; it is the continuous version of [50], Lemma 4.2, and Theorem 4.3.

Lemma 4.3. *(Properties of the exponential function on the algebra of cluster operators) The set* $L := \{t_0 I + T(t) \mid t_0 \in \mathbb{R},\ t \in \mathbb{V}\}$ *is a closed commutative subalgebra of* $B(\mathbb{H}^1)$*, containing zero as the only non-invertible element. The exponential function* $\exp(X) = \sum_{i=0}^N X^i/i!$ *is a local* C^∞*-diffeomorphism mapping onto* $L\backslash\{0\}$*. In particular,* exp *is a bijection between the sets*

$$\mathcal{T} = \{T(t) \mid t \in \mathbb{V}\} \quad \textit{and} \quad I + \mathcal{T} = \{I + T(t) \mid t \in \mathbb{V}\}.$$

The lemma also holds if $\mathbb{H}^1$ *is replaced by* $\mathbb{H}^{-1}$ *in the above, or if* $\mathbb{V}$ *is replaced by a subspace* $\mathbb{V}_d \subseteq \mathbb{V}$.

Proof. Taking Theorem 3.1 into account, the proof for the properties of L is identical with that from [50], Lemma 4.2, and Theorem 4.3. Because L is a commutative subalgebra of $\mathbb{H}^1$ resp. $\mathbb{H}^{-1}$, the exponential function is a local C^∞-diffeomorphism on $L\backslash\{0\}$, see e.g. [49]. The series terminates at $i = N$ because any product of more than N excitation operators contains more than N annihilators for the N occupied orbitals and thus has to vanish, see Lemma 2.4(iv). exp maps $\mathcal{T}$ to $I + \mathcal{T}$ by definition, and on $I + \mathcal{T}$, its inverse is given by the (terminating) logarithmic series $\log(X) = \sum_{i=1}^{N} (-1)^{i-1}(X - I)^i/i$ (see [50]), which obviously maps to $\mathcal{T}$, so the lemma is proven.

□

We can now show that under the assumptions from Section 2, the exact (weak) eigenproblem (1.1) is equivalent to the continuous Coupled Cluster equations formulated in the following theorem.

Theorem 4.4. *(The continuous Coupled Cluster equations)*

An intermediately normed function $\Psi \in \mathbb{H}^1$ *(cf. (2.8)) together with a corresponding eigenvalue* $E^* \in \mathbb{R}$ *solves the (weak, CI) eigenproblem*

$$\langle \Psi_\mu,\ (H - E^*)\Psi \rangle \ = \ 0,\ \textit{for all } \mu \in \mathcal{M} \tag{4.3}$$

if and only if $\Psi = e^T \Psi_0$ *for some cluster operator* $T = \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha$ *for which* $\|t_\alpha\|_{\mathbb{V}} < \infty$*, and which fulfils the (continuous)* unlinked Coupled Cluster equations

$$\langle \Psi_\mu, (H - E^*)e^T \Psi_0 \rangle = 0,\ \textit{for all } \mu \in \mathcal{M}, \tag{4.4}$$

or equivalently, the (continuous) linked Coupled Cluster equations,

$$E^* \ = \ \langle \Psi_0, He^T \Psi_0 \rangle,\ \langle \Psi_\mu, e^{-T} H e^T \Psi_0 \rangle = 0,\ \textit{for all } \mu \in \mathcal{M}^*, \tag{4.5}$$

that is, if $t^* := (t_\alpha)_{\alpha \in \mathcal{M}^*} \in \mathbb{V}$ *is a root of the (continuous)* Coupled Cluster function

$$f : \mathbb{V} \ \to \ \mathbb{V}',\ f(t) \ := \ \left(\langle \Psi_\alpha, e^{-T} H e^T \Psi_0 \ \rangle \right)_{\alpha \in \mathcal{M}^*}. \tag{4.6}$$

mapping $\mathbb{V}$ *to its dual* $\mathbb{V}'$ *and depending continuously on* $t \in \mathbb{V}$.

Note that the above equivalence of linked and unlinked formulation does not need to hold anymore if in a discretised setting, based on certain selection criteria, only some of the amplitudes of the discretised basis are used for a computation. In this case, $e^{T^\dagger}$ is not necessarily surjective anymore; to guarantee this, the set of selected amplitudes has to be *excitation complete*, which is for instance the case for canonical models like CCSD, CCSDT etc., see [50] for details.

Proof. Using Theorem 3.1, $\Psi \in \mathbb{H}^1$ solves the set of equations (4.3) iff there is a continuous cluster operator $S : \mathbb{H}^1 \to \mathbb{H}^1$ such that $\Psi = (I + S)\Psi_0$ and

$$\langle \Psi_\mu, (H - E^*)(I + S)\Psi_0 \rangle = 0 \text{ for all } \mu \in \mathcal{M}. \tag{4.7}$$

By Lemma 4.3, there is a unique cluster operator T such that $I + S = e^T$, so that (4.7) is equivalent to finding $T : \mathbb{H}^1 \to \mathbb{H}^1$ such that

$$\langle \Psi_\mu, (H - E^*)e^T\Psi_0 \rangle = 0, \text{ for all } \mu \in \mathcal{M}, \tag{4.8}$$

or in other words, $0 = (H - E^*)e^T\Psi_0 \in \mathbb{H}^{-1}$. By Theorem 3.1, the $\mathbb{L}_2$-adjoint $T^\dagger$ of T is continuous as mapping $\mathbb{H}^1 \to \mathbb{H}^1$; therefore, $e^{T^\dagger}$ is a continuous invertible mapping $\mathbb{H}^1 \to \mathbb{H}^1$, and (4.8) is equivalent to

$$\langle e^{-T^\dagger}\Psi, (H - E^*)e^T\Psi_0 \rangle = 0, \text{ for all } \Psi \in \mathbb{H}^1.$$

Due to the continuity of the adjoint mapping $A \mapsto A^\dagger$, we have

$$\langle e^{-T^\dagger}\Psi, (H - E^*)e^T\Psi_0 \rangle \;=\; \langle \Psi, (e^{-T^\dagger})^\dagger(H - E^*)e^T\Psi_0 \rangle \;=\; \langle \Psi, e^{-T}(H - E^*)e^T\Psi_0 \rangle$$

with the exponential e^{-T} of $-T$ taken in $\mathbb{H}^{-1}$. To show the continuity properties of the CC function, let us denote by $\langle \cdot, \cdot\cdot \rangle_{\ell_2}$ the usual $\ell_2(\mathcal{M}_k^*)$-inner product. Then, for $s, t \in \mathbb{V}$, we obtain with the boundedness of the Hamiltonian [57], Theorem 3.1, Corollary 4.2 and Lemma 4.3 that

$$\langle f(t), s \rangle_{\ell_2} \;=\; \sum_{\alpha \in \mathcal{M}^*} \langle s_\alpha \Psi_\alpha, e^{-T} H e^T \Psi_0 \rangle \;\leq\; \|T(s)\Psi_0\|_{\mathbb{H}^1} \|e^{-T} H e^T \Psi_0\|_{\mathbb{H}^{-1}} \;\leq\; C(t)\|s\|_{\mathbb{V}},$$

where the constant $C(t)$ depends on the $\mathbb{V}$-norm of t, so that $\langle f(t), \cdot \rangle_{\ell_2}$ defines a continuous functional on $\mathbb{V}$.

□

5. Concluding remarks

By the virtue of Theorem 4.4, we have obtained the continuous Coupled Cluster equations (4.4), (4.5), which are (assuming a suitable one-particle operator F exists and up to the very mild restrictions of intermediate normalization) equivalent to the original operator eigenvalue problem (1.1), the electronic Schrödinger equation: Exact eigenvectors of the eigenproblem for the Hamiltonian correspond to the solutions of the root equation for the CC function (4.6), which in the continuous context defines a nonlinear operator between the coefficient space $\mathbb{V}$ and its dual space. The CC equations (1.5) for a fixed basis set, normally used as starting point in quantum chemistry, can now be interpreted as a Galerkin discretisation of the root equation for the CC function. In the same vein, infinite dimensional generalizations of e.g. multiconfigurational CC [9, 41, 42], time-dependent CC [2,35] and of related approaches like the Jastrow ansatz [12,21,22] are desirable – also in these contexts, the traditional discrete approaches may be embedded into a functional analytic background, and new results in the theoretical investigation of these equations may be obtained hereby. Unfortunately, such generalizations usually cannot reuse many of the means utilized in the present approach for CC; rather, the specific characteristics of the respective mostly highly developed methods will have to be respected to obtain similar results; for instance, one would have to deal with the ambiguities arising in the definition of occupied and virtual space in the definition of multiconfigurational CC.
For the Coupled Cluster method, we are now in a position to treat the CC function in the formalism of nonlinear operator analysis: In a forthcoming paper [48] we will prove a local strong monotonicity for the CC function, and derive existence and uniqueness results, results concerning quasi-optimality and some results concerning error estimation.

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