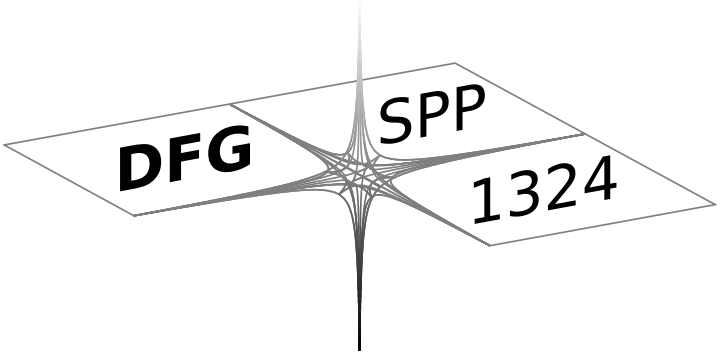
# DFG-Schwerpunktprogramm 1324

„Extraktion quantifizierbarer Information aus komplexen Systemen”

## Error Estimates for the Coupled Cluster Method

T. Rohwedder, R. Schneider

**Preprint 98**



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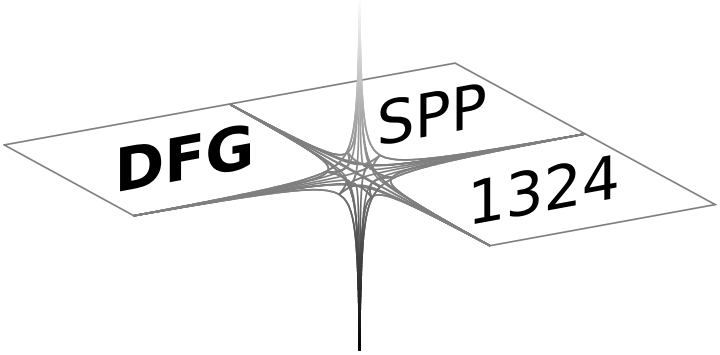

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# ERROR ESTIMATES FOR THE COUPLED CLUSTER METHOD *

Thorsten Rohwedder [1] and Reinhold Schneider [2]

**Abstract**. The Coupled Cluster (CC) method is a widely used and highly successful high precision method for the solution of the *stationary electronic Schrödinger equation*, with its practical convergence properties being similar to that of a corresponding Galerkin (CI) scheme. This behaviour has for the discrete CC method been analyzed with respect to the discrete Galerkin solution (the "full-CI-limit") in [Schneider, 2009]. Recently, we globalized the CC formulation to the full continuous space, giving a root equation for an infinite dimensional, nonlinear Coupled Cluster operator that is equivalent the full electronic Schrödinger equation [Rohwedder, 2011]. In this paper, we combine both approaches to prove existence and uniqueness results, quasi-optimality estimates and energy estimates for the CC method with respect to the solution of the full, original Schrödinger equation. The main property used is a local strong monotonicity result for the Coupled Cluster function, based on a spectral condition for the electronic Hamiltonian.

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## 1. Introduction and overview

More than 80 years after 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" [24], the development of "approximate practical methods of applying quantum mechanics", demanded by Dirac in the same breath, is still a highly active field of research at the crossroads of physics, chemistry, applied mathematics and computer science. After the development of modern day computer capacities has seen a phase

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of almost exponential growth at the end of the last century, calculations of theoretical chemistry and molecular physics have become competitive with practical experiments in the first place, or at least often allow useful predictions of empirical parameters that can assist practical investigations. On the other hand, the solution of the governing equation of quantum mechanics, the molecular Schrödinger equation, is an exceedingly high-dimensional and thus computationally demanding problem, while at the same time, an extremely high accuracy is needed in order to obtain results to be utilized in practice, so that small to medium-sized quantum chemical problems still push the limits of commonly available computational resources.

When interested in molecular properties that are mainly due to the electronic structure, or as a part of an alternating computation of electronic structure and the motion of the cores within them based on the Born-Oppenheimer approximation [13, 43], a problem of major concern is computation the electronic ground state $\underline{\Psi}$ of the system, fixing the probability distribution of $N$ electrons in the fixed field induced by the nuclei. It can be computed by solution of the stationary electronic Schrödinger equation

$$H\underline{\Psi} = E^*\underline{\Psi}, \tag{1.1}$$

a weak operator eigenvalue equation for the lowest eigenvalue $E^*$ of Hamiltonian $H : \mathbb{H}^1 \to \mathbb{H}^{-1}$ of the system as defined on the space $\mathbb{H}^1$ of antisymmetric functions of finite kinetic energy, with $H$ itself fixed by the charges and positions of the fixed nuclei. To efficiently treat the variety of practical problems covered by (1.1), it is indispensable to design highly problem-adapted methods and algorithms that balance the available computational resources against the respective required accuracy. These prerequisites have lead to a "zoo" of well-developed and often extremely sophisticated methods and algorithms for (1.1). A common approach is the formulation as the minimization problem

$$\underline{\Psi} = \mathrm{argmin}_{\Psi \in \mathbb{H}^1} \frac{\langle H\Psi, \Psi\rangle}{\langle \Psi, \Psi\rangle}, \tag{1.2}$$

followed by a restriction of the admitted solution space $\mathbb{H}^1$ to a subspace or -manifold. Minimization over anti-symmetrized rank-1-approximations, for instance, leads to the well-known Hartree-Fock ansatz [17, 30, 39, 41], or, with an empirically adopted functional, to the successful method of Density Functional Theory (DFT) [1, 25, 50, 57]. These two are probably most important methods for the qualitative study of larger systems. In subsequent post-Hartree-Fock methods, resulting solution $\Psi_0$ is also used as *reference*

*solution* for computation of a refined discrete solution $\underline{\Psi}_D = \Psi_0 + \Psi^*_D$ with an orthogonal correction $\Psi^*_D$. A straightforward such approach is a Galerkin ansatz, known as *full Configuration Interaction* ansatz in the quantum chemists' community, yielding the eigenvalue problem

$$\langle H(\Psi_0 + \Psi^*_D), \Phi_D\rangle \;=\; E\langle \Psi_0 + \Psi^*_D, \Phi_D\rangle \qquad \text{for all } \Phi_D \in \mathbb{H}^1_D \tag{1.3}$$

on an ansatz space $\mathbb{H}^1_D$ being a "full" tensor product space spanned by all possible antisymmetric products of a set of $K$ one-particle functions $\chi_I \in H^1(\mathbb{R}^3 \times \{\frac{1}{2}\})$ $\mathbb{H}^1_D$ is of the usually vast dimension $\binom{K}{N}$ (where $N$ is the number of particles, $K > N$). Therefore, to push practically relevant problems into the range of computability, it has to be truncated to some subspace $\mathbb{H}^1_d \subseteq \mathbb{H}^1_D$, usually done according to selection rules based on the excitation level of the basis function [30], resulting in a "truncated CI" method. This approach shares the enjoyable analytic properties of the Galerkin method applied to symmetric eigenvalue problems [16], i.e. the method is variational and we have quasi-optimality estimates for the approximation error with respect to the real solution $\underline{\Psi} = \Psi_0 + \Psi^*$ of (1.1), (1.2), being of the form

$$\|\Psi^*_d - \Psi^*\| \;\lesssim\; d(\mathbb{H}^1_d, \Psi^*), \quad E(\underline{\Psi}^*_d) - E^* \;\lesssim\; \|\Psi^*_d - \Psi^*\|^2 \;\lesssim\; d(\mathbb{H}^1_d, \Psi^*)^2, \tag{1.4}$$

with distances measured with respect to the $\mathbb{H}^1$-norm, see also [64] for more refined estimates. In contrast to these nice theoretical properties is a mayor practical shortcoming of CI: The above truncation step makes the resulting CI calculation on the subspace $\mathbb{H}^1_d \subseteq \mathbb{H}^1_D$ non-size-consistent [6,8,48], by which we mean that the separability conditions

$$\Psi^*_{d,A+B} \;=\; \Psi_{d,A} \wedge \Psi_{d,B}, \qquad E(\Psi^*_{d,A+B}) \;=\; E(\Psi^*_{d,A}) \wedge E(\Psi^*_{d,B})$$

relating the antisymmetrized product of solutions $\Psi_{d,A}, \Psi_{d,B}$ for two noninteracting systems $A, B$ to the solution $\Psi^*_{d,A+B}$ for the comprised system are in general *not* fulfilled for CI. This deficiency leads e.g. to inappropriate dissociation curves in the description of reaction mechanisms and renders the CI method useless in many practical applications. The Coupled Cluster (CC) approach, introduced in the field of atomic physics [19,20,36,62] and later used on problems of quantum chemistry (see [18]), remedies this shortcoming by replacing the linear ansatz of full CI by an *exponential* parametrization of the sought

solution $\underline{\Psi}_D$, i.e. it reformulates

$$\underline{\Psi}_D \;=\; \underbrace{\Psi_0 + \Psi_D^* \;=\; \Psi_0 + \sum_{\mu\in\mathcal{M}_D} c_\mu \Psi_\mu}_{\text{CI ansatz}} \;=\; \underbrace{e^{T(t_D)}\Psi_0}_{\text{CC ansatz}}$$

for a coefficient vector $t_D = (t_{\mu_D})_{\mu_D\in\mathcal{M}_D}$, determining a corresponding *cluster operator* $T(t_D)$ (see Section 2 for details). After additionally inserting $e^{-T(t_D)}$ (see [56]), this ansatz leads to a nonlinear equation

$$f(t_D) \;=\; \langle \Psi_{\mu_D}, e^{-T(t_D)} H e^{T(t_D)} \Psi_0 \rangle = 0 \qquad \text{for all } \Psi_{\mu_D} \perp \Psi_0 \tag{1.5}$$

for $t_D$, and $\underline{\Psi}_D = e^{T(t_D)}\Psi_0$ corresponds to the full CI-solution of (1.3). Equation (1.5) has two main features: First of all, truncation of this equation to a reduced Galerkin space gives a set of equations that (in contrast to truncated CI) *still is size-consistent*, resulting in the computation of $t_d = (t_{\mu_d})_{\mu_d\in\mathcal{M}_d}$, $\mathcal{M}_d \subseteq \mathcal{M}_D$ such that

$$f(t_d) \;=\; \langle \Psi_{\mu_d}, e^{-T(t_d)} H e^{T(t_d)} \Psi_0 \rangle = 0 \qquad \text{for all } \Psi_{\mu_d} \perp \Psi_0. \tag{1.6}$$

From the solution of this Galerkin projection, the corresponding CC energy $E_d$ can then be computed. As second feature, the operator $e^{-T(t_d)} H e^{T(t_d)}$ can be expanded in the so-called Baker-Campbell-Haussdorff series, which terminates due to the structure of $H$ , $f(t_d)$ so that can be evaluated exactly within a given finite basis set, being a fourth-order polynomial in the coefficients $t_{\mu_d}$ of $t_d$. Nevertheless, implementation of the evaluation of $f$ is a complicated matter of its own owed to the difficult incorporation of antisymmetry constraints imposed on the solution space $\mathbb{H}^1$, cf. Sec.A for more practical remarks.

Regardless of this practical difficulties which have been overcome during the last decades, the CC method has, due to its favourable properties of size-consistency and an often quite favourable convergence behaviour, become the probably most widely applied tool in the calculation of ground state solutions of the stationary $N$-electron Schrödinger equation when high-accuracy results are demanded. In the variant of the CCSD(T) method [53], 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 [42], which is why CCSD(T) is often referred to as the "golden standard of quantum chemistry". The Coupled Cluster method even usually outperforms the CI method of corresponding scaling, see e.g. [21, 31, 34]. When computing different levels of approximation $\underline{\Psi}_d$ to a discrete full-CI solution $\underline{\Psi}_D$ for well-behaved examples, the

energies are often observed to converge quadratically with respect to the energy error of the cluster amplitude vectors $\|t_d - t_D\|_{\mathbb{V}}$ in analogy to the right hand equation of (1.4). For reviews on Coupled Cluster theory, see [7,37] and the abundance of references given therein, as well as the article [12] for a broader scope on the applications in physics; for some recent developments, see [10,15,33,35,44,45,59]. As successful as the history of CC

calculations may be, it is contrasted by a scarcity of theoretical results underpinning this behaviour in terms of numerical analysis. To the authors' knowledge, the only existence and uniqueness results are those for the discrete equations given in [58], while there are no results on the convergence of the exact, continuous equations; a first error bound for the convergence of the energies to the *discrete* "full-CI energy" was given in [34], where Werner Kutzelnigg derives the estimate

$$|E_d - E_D| \lesssim \|\Psi_d^* - \Psi_D^*\| \, \|\Psi_d^*\| \;\sim\; \|t_d - t_D\| \, \|t_d\|. \tag{1.7}$$

Comparing this with what is known for the CI method (1.4), this estimate is unsatisfactory in view of the practical superiority of the CC method, and methodological improvements have also already been suggested in [34]. In this paper, we will use tools from numerical analysis to prove estimates similar to those in (1.4), showing that also from a theoretical point of view, the CC method behaves similar to the CI method. To do so, three peculiarities of the classical formulation of the CC approach have to be taken into account:

**(i)** CC, in its classical formulation, is a *finite dimensional theory* as reformulation of the full CI-approach, that is, as a nonlinear equation for coefficients in a fixed, *discretized* basis set. In a previous publication [56], we showed that under appropriate assumptions, the original full electronic Schrödinger equation (1.1) can also be reformulated *equivalently* as a root equation for a *continuous Coupled Cluster function*

$$f : \mathbb{V} \;\to\; \mathbb{V}', \;\; f(t) \;:=\; \big(\langle \Psi_\alpha, e^{-T(t)} H e^{T}(t) \Psi_0 \, \rangle\big)_{\alpha \in \mathcal{M}^*}, \tag{1.8}$$

where $f$ is defined on a coefficient space $\mathbb{V}$ corresponding to the full continuous space $\mathbb{H}^1$, and that the discrete CC equations (1.6) can be viewed as Galerkin discretizations of (1.8). Using these results, we may thus rely on the machinery of operator analysis to obtain direct quasi-optimality estimates with respect to the solution $t^*$ of (1.8), corresponding to the full solution $\Psi = e^{T(t^*)}\Psi_0$.

**(ii)** CC, in its classical formulation, is *non-variational*, so that one cannot expect estimates for the CC energy that take the simple form as for CI, (1.4). Instead, an approach put forward by Rannacher and coworkers [5,9], tailored for goal-oriented estimates for non-symmetric eigenvalue problems and nonsymmetric constrained minimization problems, offers the appropriate tool. Here, a *dual solution* $z^*$ and its discrete counterpart $z_d$ enter the estimates. For the discrete case, we already used this approach in [58] to show that

$$|E_d - E_D| \lesssim (\|t_d - t_D\|_{\mathbb{V}_d} + \|z_d - z_D\|_{\mathbb{V}_d})^2 \tag{1.9}$$

holds for the discrete energies $E_d, E_D$ if the CC approach is based on eigenfunctions of a discrete Fock operator. Alas, this condition excludes many of the more sophisticated CC approaches; also, all estimates in [58] are given with respect to the full CI (discrete) solution, and then connected to the full, continuous solution of (1.1) using the quasi-optimality of the CI-method and certain uniformity conditions, and we will also avoid this detour here.

We will in this work combine the approaches outlined in (i) and (ii): First, we analyze the continuous CC function and interpret the discrete CC equations (1.6) as discretizations of $f$. We directly derive from this results for the convergence towards the full solution of (1.1) analogous to (1.4), that is

$$\|t_d - t^*\|_{\mathbb{V}} \lesssim d(\mathbb{V}_d, t^*),\ |E(t_d) - E^*| \lesssim (\|t_d - t^*\|_{\mathbb{V}} + \|z_d - z^*\|_{\mathbb{V}})^2 \lesssim d(\mathbb{V}_d, \{t^*, z^*\})^2,$$

in which $\|t\|_{\mathbb{V}}$ denotes a weighted $\ell_2$-norm on the coefficient space $\mathbb{V}$ as above, equivalent to the $\mathbb{H}^1$-norm of $\|\sum_\mu t_\mu \Psi_\mu\|$. Also, we will prove certain existence and uniqueness statements for the continuous as well as the discrete CC equations. The assumptions under which these results hold are fixed by the physical properties of the system under consideration: We assume that (a) the lowest eigenvalue of $H$ is simple and isolated from the rest of the spectrum by a nonzero gap $\gamma$, and (b) the existence of a sufficiently good antisymmetrized rank-1 approximation (reference solution) $\Psi_0$, constructed from a basis of an invariant subspace of a one-particle operator as for instance the Fock operator of the system (also cf. the remarks in Sec. 2). We will show that this guarantees that the Coupled Cluster function is strongly monotone on a neighbourhood of the primary solution $t^*$, which then (corresponding to the property of ellipticity for linear equations) implies existence and uniqueness statements and quasi-optimality estimates. The analysis will also underpin the particular importance of two constants for the practical convergence behaviour of the Coupled Cluster method as well as for the quasi-optimal convergence to

the full solution, namely the quality of the reference determinant as measured by $\|\Psi_0 - \underline{\Psi}\|$, and spectral gap $\gamma$ of the Hamiltonian.
The rest of the paper is organized as follows: In Section 2, we will mainly review the content of the previous [56] as far as it is relevant for this work: The reformulation of the electronic Schrödinger equation (1.1) as a root equation for the continuous CC equations (1.8) will be introduced at more length, and some important supplementary results needed here will be compiled. Also, we will give a mathematically waterproof formulation of the above mentioned assumptions this work is based on. In Section 3, the analytical properties of the CC function as operator between the coefficient space $\mathbb{V}$ and its dual are analyzed; the main result is its strong monotonicity on a neighbourhood of the solution (Theorem 3.2). The existence and uniqueness statements and quasi-optimality results for the CC method discussed above are then strictly derived in from this Section 4, see Theorems 4.1 and 4.5. Section (A) discusses some aspects concerned with the practical treatment of the CC equations (1.6) from the viewpoint given in this work. Some concluding remarks are given in Section 5.

## 2. Preliminaries: From the Schrödinger equation to CC. Basic assumptions.

In this section, we fix the mathematical framework needed for the due analysis: In part (i), we introduce our basic notation for the Schrödinger equation (1.1). Parts (ii) and (iii) give an overview of the transition to the continuous Coupled Cluster formulation for this equation, mainly taken from our previous work [56] (with a "continuous CI method" an intermediate stage). Part (iv) contains some important supplementary results, partly taken from [56], that will also be needed later. Along the way, the three basic assumptions made in this work are introduced.

**(i) Electronic Schrödinger equation; first basic assumption.** The goal of electronic structure calculations is solution of the $N$-particle electronic Schrödinger equation. It can be stated as a weak operator eigenvalue equation on a suitable solution space $\mathbb{H}^1$, which can be defined either as the space

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

where $\mathbb{L}^2$ denotes the antisymmetric functions from $L^2((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N)$ and $H^1(\Omega)$ denotes the Sobolev space of one time weakly differentiable functions over a given measure space $\Omega$,

or alternatively as a subspace of (2.1) that is an eigenspace of an operator commuting with $H$. The latter results in a restricted, often computationally less demanding, formulation on this subspace; in practice, the use of a fixed eigenspace of the $z$-spin operator defined on (2.1) is rather common. On such a fixed space $\mathbb{H}^1$, we wish to solve the weak eigenvalue problem

$$\langle (H - E^*)\underline{\Psi}, \Phi \rangle \;=\; 0 \qquad \text{for all} \quad \Phi \in \mathbb{H}^1 \tag{2.2}$$

for the lowest eigenvalue $E^*$ of the $N$-electron Hamiltonian $H : \mathbb{H}^1 \to \mathbb{H}^{-1}$,

$$H := \sum_{i=1}^{N} \Delta_i \;+\; \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{1}{|x_i - x_j|} \;-\; \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k}{|x_i - R_k|}. \tag{2.3}$$

In this, the Laplacian $\Delta_i$ acts on the $i$-th spatial component $x_i \in \mathbb{R}^3$ of a wave function $\Psi = \Psi\big((x_1, s_1), \ldots, (x_n, s_n)\big)$, and the constants $Z_k \in \mathbb{N}$, $R_k \in \mathbb{R}^3$ are the charges and positions of the $M$ fixed nuclei. $H$ is bounded and fulfils a Gårding inequality [63] on $\mathbb{H}^1$ [64]: There holds

$$c\, \|\Psi\|^2 - \mu \langle \Psi, \Psi \rangle \;\leq\; \langle H\Psi, \Psi \rangle; \qquad\qquad \langle H\Psi, \Phi \rangle \;\leq\; \overline{\Lambda}\, \|\Psi\|\, \|\Phi\| \tag{2.4}$$

for all $\Psi, \Phi \in \mathbb{H}^1$ and constants $\mu \in \mathbb{R}$, $c, C > 0$. In the formulation of (2.2), the existence of a smallest eigenvalue is supposed; for the analysis to be performed in this work, we will make the following stronger assumption on the spectrum of $H$:

**Assumption I.** *The number*

$$\mathcal{E}^* \;:=\; \inf\{\, \langle H\Psi, \Psi \rangle \mid \Psi \in \mathbb{H}^1,\; \|\Psi\| = 1 \,\} \tag{2.5}$$

*fulfils*

$$\mathcal{E}^* \;<\; \inf \mathrm{spec}_{ess}(H) \tag{2.6}$$

*(thus, $\mathcal{E}^* = E^*$), and is a single eigenvalue of $H$.*

The bottom $\inf \mathrm{spec}_{ess}$ of the essential spectrum can be associated with a formalization of the ionization threshold energy of the molecule (see e.g. [2, 51, 64]). The inequality (2.6) therefore follows [64] if we can assume that for the given configuration of nuclei (as expressed in $H$), it is energetically more advantageous for the electrons to stay in the

vicinity of the nuclei than to fade away at infinity – which is physically reasonable if we want to compute stable molecules. The valitity of (2.6) can be formally proven for some cases, e.g. for one-atomic molecules or under certain conditions on the total charge of the molecules. For a review and the related HVZ-theorem, confer [60] or the quite exhaustive review [32] and the references therein. As per the second requirement contained in Assumption I, i.e. that $E^*$ be a simple eigenvalue, results are quite scarce to our best knowledge. We note though that even in the case of hydrogen, there are two identical solutions of spin up and spin down, respectively, if the full space (2.1) is considered, while restriction to eigenspaces of the $z$-spin operator yields two identical problems with simple lowest eigenvalues. We therefore stress that the whole analysis in this paper also holds for CC equations formulated on these subspaces of fixed $z$-spin, and that these restricted calculations are actually what is almost exclusively computed in practice due to the computational savings earned from the restriction.

**(ii) The complete CI equations; second and third basic assumption.** For reformulation of the eigenvalue equation (2.2) in terms of the Coupled Cluster equations, a basis $\mathbb{B}$ of the space $\mathbb{H}^1$ now has to be fixed. We construct $\mathbb{B}$ from a complete *one-particle* basis

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

of the one-electron state space

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

indexed by ordered an set $\mathcal{I}$ in the following way. For $\mathbb{H}^1$ given by (2.1), we obtain a *Slater basis* of $\mathbb{H}^1$ by letting

$$\mathbb{B} \;:=\; \{\Psi_\mu \mid \mu \in \mathcal{M}\}, \qquad \Psi_\mu \;:=\; \bigwedge_{i=1}^{N} \chi_{P_i} \;:=\; \mathcal{Q}(\otimes_{i=1}^{N} \chi_{P_i}), \tag{2.7}$$

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

$$\mathcal{Q}\Psi = \frac{1}{\sqrt{N!}} \sum_{\pi \in S(N)} (-1)^{\mathrm{sgn}(\pi)} \Psi((x_{\pi(1)}, s_{\pi(1)}), \ldots, (x_{\pi(N)}, s_{\pi(N)})), \tag{2.8}$$

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

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

If $\mathbb{H}^1$ is given by a subspace of (2.1), corresponding to an eigenspace of the $z$-spin operator, $B$ is chosen as an eigenbasis of the one-electron $z$-spin operator $S_z$; (2.7) then is an eigenbasis of $S_z$ and can be restricted accordingly (see [55] for an explicit construction). To obtain a well-defined infinite-dimensional Coupled Cluster theory as developed in [56] as foundation stone for the analysis in this paper, we will make the same assumptions as in this work, that is, we suppose that the *reference determinant*

$$\Psi_0 \ := \ \bigwedge_{i=1}^{N} \chi_{I_i}, \tag{2.9}$$

consists of functions spanning an eigenspace of a suitable one-particle operator $F$ and approximates the sought eigenfunction $\Psi$ to some extent.

**Assumption II.** *A subset*

$$B_{occ} \ := \ \{\chi_{I_1}, \ldots, \chi_{I_N}\} \ \subseteq \ B \tag{2.10}$$

*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*

$$\gamma \ \langle \varphi, \varphi \rangle_1 \ \leq \ \langle F\varphi, \varphi \rangle \ \leq \ \Gamma \ \langle \varphi, \varphi \rangle_1 \quad \textit{for all} \quad \varphi \in H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\}). \tag{2.11}$$

In the above, $B_{\mathrm{occ}}$ may e.g. be an eigenbasis of a continuous or discrete Fock or Kohn-Sham operator $F$, which can then be accompanied by an arbitrary basis spanning the orthogonal complement span$B_{\mathrm{occ}}^{\perp}$ to obtain the full basis $B$; Assumption II is therefore fulfilled for a broad range of relevant problems and various practical variants of the CC scheme, see [56] for more details. In particular, it also allows to formulate the continuous CC approach (Theorem (2.3)) based on a discrete reference determinant.
Additionally, we make an assumption on the quality of the reference determinant:

**Assumption III.** *The reference determinant (2.9) formed from $B_{occ}$ approximates the full solution $\Psi$ to a certain extent, so that for $\Psi^* = \Psi_0 - \Psi$,*

$$\|\Psi^*\| < \epsilon \tag{2.12}$$

*with $\epsilon$ specified later. In particular, the nonorthogonality assumption*

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

*holds.*

A reference $\Psi_0 \not\perp \underline{\Psi}$ fixed, equation (2.2) can be reformulated in terms of the Configuration Interaction ansatz: "Find $\underline{\Psi} = \Psi_0 + \Psi^* \in \mathbb{H}^1$ such that

$$\langle H(\Psi_0 + \Psi^*), \Psi_\mu \rangle \ = \ E\langle \Psi_0 + \Psi^*, \Psi_\mu \rangle \quad \text{for all} \quad \Psi_\mu \in \mathbb{B}, \quad \text{where} \quad \Psi^* \perp \Psi_0." \quad (2.13)$$

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

$$\langle \underline{\Psi}, \Psi_0 \rangle \ = \ 1 \quad (2.14)$$

is fulfilled, and also orthogonal (due to Assumption II) in the inner product induced by the lifted Fock operator $F^N$, equivalent to that on $\mathbb{H}^1$ [55]. Although this norm will not play a major role in the estimates in this work, we note that it provides the basis for the energy-space construction of the continuous CC formulation in [56] and enters the continuity estimates for the cluster operator $T$, see Theorem 2.4.

**(iii) Excitation and cluster operators; the coefficient space $\mathbb{V}$; the continuous Coupled Cluster equations.** In Coupled Cluster theory, Equation (2.13) is now reformulated by an exponential ansatz in terms of so-called cluster operators. To do so, we now introduce excitation and cluster operators by which the CC equations are formulated, and introduce a coefficient space $\mathbb{V}$ reflecting the set of admittable corrections $\Psi^* \in \mathbb{H}^1$; we then can formulate the continuous CC equations. In the introduction of excitation and cluster operators and in the following, we will make use of the following notations.

**Notations 2.1.**

(i) *Functions $\chi_I \in B_{occ}$ from (2.10) are called* occupied orbitals. *Following conventions of quantum chemistry literature, we index them by letters $I, J, K, \ldots \in occ$; functions $\chi_A \in B \backslash B_{occ}$ are called* virtual orbitals, *denoted by $A, B, C, \ldots \in virt$. Undistincted indices are denoted as $P, Q, R$, etc.*

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

(iii) *If for* $\mu = (P_1, \ldots, P_N) \in \mathcal{M}$, $P \in \mathcal{I}$, *there holds* $P \in \{P_1, \ldots, P_N\}$, *we write* $P \in \mu$ *and say* $P$ *is contained in* $\mu$.

(iv) *For two multi-indices* $\nu, \mu \in \mathcal{M}$, *we write* $\mu \subseteq \nu$ *iff for all* $I \in occ$, $I \in \mu$ *implies* $I \in \nu$ *and for all* $A \in virt$, $A \in \nu$ *implies* $I \in \mu$. *(This means that* $\nu$ *can be constructed from* $\mu$ *by exchanging some of the occupied orbitals in* $\mu$ *against virtuals.)*

(v) *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* $\nu = \mu \oplus \alpha$, $\alpha = \nu \ominus \mu$.

The CC approach is formulated in terms of *excitation operators* $X_\mu$, defined for each index $\mu \in \mathcal{M}^*$ in terms of *annihilation and creation operators*. Because this formalism is not needed in the context persued here, we refer the interested reader to the Appendix where the according definitions and some references are given. Here, we give the following characterization of $X_\mu$ by their action on any basis function $\Psi_\nu \in \mathbb{B}$.

**Definition 2.2.** *(Excitation operators.) Let* $\mu \in \mathcal{M}^*, \nu \in \mathcal{M}$, $\mu = (I_{r+1}, \ldots, I_N, A_1, \ldots, A_r)$ *with* $I_{r+1}, \ldots, I_N \in occ$, $A_1, \ldots, A_r \in virt$. *We define that if* $I_{r+1}, \ldots, I_N \in \nu$,

$$X_\mu \Psi_\nu = \pm \Psi_{\mu \oplus \nu},$$

*with the sign* $\pm$ *uniquely determined (see [56]); that is, the operator* $X_\mu$ *acts on such a basis function* $\Psi_\nu$ *by replacing* $I_{r+1}, \ldots, I_N$ *by the virtual orbitals* $A_1, \ldots, A_r$. *If* $I_i \notin \nu$ *for some* $1 \leq i < r$, *we let*

$$X_\mu \Psi_\nu = 0.$$

*By linear continuation, we obtain a continuous linear operator*

$$X_\mu : \mathbb{L}_2 \to \mathbb{L}_2,$$

*called the excitation operator belonging to the index* $\mu$.

Note that by definition, excitation operators commute,

$$X_\mu X_\nu \;=\; X_{\mu \oplus \nu} \;=\; X_{\nu \oplus \mu} \;=\; X_\nu X_\mu,$$

an essential prerequisite for the exponential ansatz in CC. Because trivially, $X_\mu \Psi_0 = \Psi_\mu$ for each index $\mu \in \mathcal{M}^*$, every intermediately normed function $\Psi = \Psi_0 + \Psi^* \in \mathbb{L}^2$ can be

expressed as

$$\Psi \;=\; \Psi_0 + \Psi^* \;=\; \Psi_0 + \sum_{\mu\in\mathcal{M}^*} t_\mu \Psi_\mu \;=\; \Psi_0 + \sum_{\mu\in\mathcal{M}^*} t_\mu X_\mu \Psi_0 \;=:\; (I + T(t))\Psi_0 \quad (2.15)$$

with the operator $T(t)$ the *cluster operator* belonging to the coefficient vector $(t_\mu)_{\mu\in\mathcal{M}}$ of $\Psi^*$.

By definition of the Schrödinger equation (2.2) resp. its CI form (2.13), we are looking for a correction $\Psi^* = \sum_{\alpha\in\mathcal{M}^*} t_\alpha \Psi_\alpha$ contained in the space $\mathbb{H}^1$. In terms of the corresponding vector $t = (t_\mu)_{\mu\in\mathcal{M}}$, this restriction can be formulated by defining a subspace $\mathbb{V} \subseteq \ell_2(\mathcal{M}^*)$ by

$$\mathbb{V} \;:=\; \{t \in \ell_2(\mathcal{M}^*) \mid \|t\|_{\mathbb{V}} < \infty\}. \quad (2.16)$$

where

$$\langle t, s\rangle_{\mathbb{V}} \;:=\; \langle \sum_{\alpha\in\mathcal{M}^*} t_\alpha \Psi_\alpha, \sum_{\beta\in\mathcal{M}^*} s_\beta \Psi_\beta\rangle^2_{\mathbb{H}^1}, \qquad \|t\|_{\mathbb{V}} \;:=\; \langle t, t\rangle^{1/2}_{\mathbb{V}}. \quad (2.17)$$

Note that $\mathbb{V}$ is a Hilbert space, and that $t \in \mathbb{V}$ iff $\Psi^* = \sum_{\mu\in\mathcal{M}^*} t_\mu \Psi_\mu \in \mathbb{H}^1$. Using this definition, we can formulate the main result of [56], which embeds the canonical (finite-dimensional) CC equations (1.6) in a functionalanlytical context. Thus, aside from the classical interpretation of CC as an approximation of a finite-dimensional Galerkin ("full-CI") limit, we can also view the canonical CC equations as an approximation of the continuous CC function as a Galerkin scheme for the conituous Coupled Cluster function $f$, and analyse by according methods its convergence behaviour towards full the solution $(\underline{\Psi}, E^*)$ of the full electronic Schrödinger equation (1.1).

**Theorem 2.3.** *(The continuous Coupled Cluster equations)*

*(i) Let $B$ be a one-particle basis which fulfils Assumption II, $\mathbb{B}$ the according antisymmetric basis for the solution space $\mathbb{H}^1$. An intermediately normed function $\underline{\Psi} \in \mathbb{H}^1$ (cf. (2.14)) together with a corresponding eigenvalue $E^* \in \mathbb{R}$ solves the eigenproblem*

$$H\underline{\Psi} = E^*\underline{\Psi} \quad (2.18)$$

*if and only if*

$$\underline{\Psi} = e^T \Psi_0$$

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

$$\langle \Psi_\mu, e^{-T(t^*)} H e^{T(t^*)} \Psi_0 \rangle = 0 \text{ for all } \mu \in \mathcal{M}^*, \qquad E^* = \langle \Psi_0, H e^{T(t^*)} \Psi_0 \rangle, \tag{2.19}$$

*that is, if* $t^* = (t_\alpha)_{\alpha\in\mathcal{M}^*} \in \mathbb{V}$ *is a root of the (continuous)* Coupled Cluster function[1]*,*

$$f : \mathbb{V} \to \mathbb{V}',\ f(t) := \big( \langle \Psi_\alpha, e^{-T(t)} H e^{T(t)} \Psi_0 \rangle \big)_{\alpha\in\mathcal{M}^*} = 0 \in \mathbb{V}' \tag{2.20}$$

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

*(ii) Let* $\mathbb{B}_d = \{\Psi_\mu | \mu \in \mathcal{M}_d\} \subseteq \mathbb{B}$ *a basis set for which* $\Psi_0 \in \mathbb{B}_{disc}$*, and denote the corresponding coefficient space by* $\mathbb{V}_d \subseteq \mathbb{V}$*. The Galerkin projection of the continuous CC equation (2.20), given by the set of equations*

$$\langle s_d, f(t_d) \rangle = 0 \text{ for all } s_d \in \mathbb{V}_d, \qquad E_d = \langle \Psi_0, H e^{T(t_d)} \Psi_0 \rangle, \tag{2.21}$$

*to be solved for* $t_d \in \mathbb{V}_d$*, or in terms of wavefunctions,*

$$\langle \Psi_\mu, e^{-T(t_d)} H e^{T(t_d)} \Psi_0 \rangle = 0 \text{ for all } \mu \in \mathcal{M}_d, \qquad E_d = \langle \Psi_0, H e^{T(t_d)} \Psi_0 \rangle, \tag{2.22}$$

*then corresponds to the classical, finite-dimensional CC equations, based on the reference determinant* $\Psi_0$ *and the trial space* $\mathbb{T}_d = span\mathbb{B}_d$*.*

For the proof of the fact that $f$ maps $\mathbb{V} \to \mathbb{V}'$ continuously, cf. Lemma 3.1.

**(iv) Supplementary results.** Some more technical results will be needed in this work, and we compile them here to refer to them later. For the proof of Theorem 2.4, see [56].

**Theorem 2.4.** *(The algebra of* $\mathbb{H}^1$*-continuous cluster operators)*

(i) *Let* $\Psi^* = \sum_{\alpha\in\mathcal{M}^*} t_\alpha \Psi_\alpha \in \mathbb{H}^1$*,* $t = (t_\alpha)_{\alpha\in\mathcal{M}^*} \in \mathbb{V}$ *the corresponding coefficient vector. There holds*

$$\|T\|_{\mathbb{H}^1\to\mathbb{H}^1} \sim \|\Psi^*\| \sim \|t\|_{\mathbb{V}}, \qquad \|T^\dagger\|_{\mathbb{H}^1\to\mathbb{H}^1} \leq \|\Psi^*\| \sim \|t\|_{\mathbb{V}}, \tag{2.23}$$

*where the constants involved depend only on the number* $N$ *of electrons, on the constants in (2.11) and on* $\|\Psi_0\|$*.*

[1]The Coupled Cluster function is defined on the infinite dimensional space $\mathbb{V}$, and some readers might therefore prefer the term "(nonlinear) operator" and denote it by a capital letter. To keep consistent with quantum chemistry literature and to avoid confusion with the "Fock operator-like" mapping $F$, we will stick to the physicist's/chemist's nomenclature of "the Coupled Cluster function" $f$ here.

(ii) *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 locally Lipschitz continuous local* $C^\infty$*-diffeomorphism mapping* $L$ *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* $\mathbb{V}_d \subseteq \mathbb{V}$*.*

The following lemma shows that from (2.4), it follows that $H - E_0$ is a bounded, $\mathbb{H}^1$-elliptic mapping on the orthogonal complement of the eigenspace belonging to $E_0$. This fact lays the basis for the monotonicity of the Coupled Cluster function, on which in turn the whole error analysis given here will be based.

**Lemma 2.5.** *(Ellipticity results for* $H$*)*

(i) *Let* $V \hookrightarrow X \hookrightarrow V'$ *be a Gelfand triple, and let* $A : V \to V'$ *be a symmetric operator which is bounded from below by a Gårding estimate*

$$\langle Av, v\rangle \ \geq\ c\|v\|_V^2 \ -\ \mu\|v\|_X^2 \tag{2.24}$$

*with constants* $c > 0, \mu \in \mathbb{R}$*. If additionally,* $A$ *is* $X$*-elliptic, i.e.*

$$\langle Av, v\rangle \ \geq\ \gamma\|v\|_X^2 \textit{ for all } v \in V \tag{2.25}$$

*for some* $\gamma > 0$*, then* $A$ *is also* $V$*-elliptic, i.e. for some* $\gamma' > 0$*,*

$$\langle Av, v\rangle \ \geq\ \gamma'\|v\|_V^2 \textit{ for all } v \in V. \tag{2.26}$$

(ii) *If (2.25) only holds on a closed subspace* $U \subseteq V$*, this still implies*

$$\langle Au, u\rangle \ \geq\ \gamma'\|u\|_V^2 \textit{ for all } u \in U. \tag{2.27}$$

*Proof.* To prove (i), we let $q := \gamma/(\mu + \gamma) < 1$ and use that $\langle Av, v\rangle$ can be expressed as

$$q\langle Av, v\rangle \ +\ (1-q)\langle Av, v\rangle \ \geq\ qc\|v\|_V^2 \ +\ (\gamma - q(\mu+\gamma))\|v\|_X^2 \ =\ qc\|v\|_V^2.$$

To prove statement (ii), we denote the projector on $U$ by $P$; the restriction $\tilde{A} = PAP$ is symmetric and fulfils the conditions (2.24), (2.25) with $A$ replaced by $\tilde{A}$, $V$ replaced by

$U$. Part (i) thus implies

$$\langle \tilde{A}u, u\rangle \;\geq\; \gamma' \|u\|_V^2 \qquad \text{for all } u \in U, \tag{2.28}$$

which gives (2.27).

□

## 3. Analytical properties of the Coupled Cluster function

In this section, we derive various analytical results for the Coupled Cluster function that are the main tools to the estimates for the CC method given in Section 4. In (i), these results are compiled in Lemma 3.1, Theorem 3.2 and Corollary 3.3. The proof for the main result of locally strongly monotonicity (Theorem 3.2) is performed in (ii). In (iii), we added some results on the convergence of quasi-Newton methods that are often used for practical solution of the CC equations.

**(i) Main statements on the CC function $f$.** We start by the next lemma compiling some general properties of $f$, which were already shown in [58] for the discrete case.

**Lemma 3.1.** *(The Coupled Cluster function)*

*The Coupled Cluster function*

$$f : \mathbb{V} \;\to\; \mathbb{V}',\; f(t) \;:=\; \left(\langle \Psi_\alpha, e^{-T(t)} H e^{T(t)} \Psi_0 \,\rangle\right)_{\alpha \in \mathcal{M}^*} \tag{3.1}$$

*is a $C^\infty$-mapping from $\mathbb{V}$ to its dual $\mathbb{V}'$. $f$ and all derivatives $f^{(n)}$ of $f$ are Lipschitz-continuous on bounded domains of $\mathbb{V}$. The respective constants are uniform for all Coupled Cluster methods that fulfil the estimates (2.11) (Assumption II) and (2.12) (Assumption III) uniformly.*

*Proof of Lemma 3.1.* Let us denote by $\langle \cdot, \cdot \rangle_{\ell_2}$ the usual $\ell_2(\mathcal{M}_k^*)$-inner product. Then, for $s, t \in \mathbb{V}$, we obtain with the use of (2.4) and Theorem 2.4, that

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

where it follows from Theorem 2.4 the constant $C$ depends on $\|t\|_{\mathbb{V}}$, $N$, the constants in the spectral equivalence (2.11) for $F$, and on $\|\Psi_0\| \leq \epsilon + C$. $\langle f(t), \cdot \rangle_{\ell_2}$ thus defines a continuous functional on $\mathbb{V}$. In particular, the Lipschitz continuity of $f$ on bounded domains follows from a short calculation based on the same property of $T \mapsto e^T$ as

mapping $\mathbb{H}^1 \to \mathbb{H}^1$ and $\mathbb{H}^{-1} \to \mathbb{H}^{-1}$, see Theorem 2.4(ii). $f$ is $C^\infty$ as a composition of $C^\infty$-functions. For the proof that all derivatives of $f$ are Lipschitz-continuous on bounded domains, see [58] which transfers to our case.

□

The following is the main result used in the proof of the error estimates and optimality results in Section 4.

**Theorem 3.2.** *(Local strong monotonicity of the CC function)*

*Let $f$ denote a CC function based on a Hamiltonian $H$ fulfilling Assumption I and a reference $\Psi_0$ fulfilling Assumptions II and III. The Coupled Cluster function $f$ then is strongly monotone in a neighbourhood of its solution $t^* = (t^*_\alpha)_{\alpha\in\mathcal{M}^*}$, i.e. there are constants $\gamma, \delta > 0$ such that*

$$\langle f(s) - f(t), s - t\rangle \;\geq\; \gamma \cdot \|s - t\|^2_{\mathbb{V}} \tag{3.2}$$

*holds for all $s, t \in \mathbb{V}$ with $\|s - t^*\|_{\mathbb{V}}, \|t - t^*\|_{\mathbb{V}} < \delta$. $H$ fixed, the constants are uniform for all Coupled Cluster methods that fulfil the estimates (2.11) and (2.12) uniformly.*

We defer the proof for a moment (see (ii)), and first note:

**Corollary 3.3.** *(Properties of the derivative of $f$)*

*Let the assumptions of Theorem 3.2 hold. For $s \in U_\delta(t^*)$, the derivatives $Df(s) \in L(\mathbb{V}, \mathbb{V}')$ of the Coupled Cluster function $f$ at $s$ are uniformly bounded, $\mathbb{V}$-coercive linear operators, i.e. there is a $C > 0$ such that*

$$\langle Df(s)u, v\rangle \;\leq\; C \cdot \|u\|_{\mathbb{V}}\|v\|_{\mathbb{V}}, \qquad \langle Df(s)u, u\rangle \;\geq\; \gamma\|u\|^2_{\mathbb{V}} \tag{3.3}$$

*holds for all $s \in U_\delta(t^*)$, $u, v \in \mathbb{V}$ (with $\gamma$ from (3.2)).*

*Proof.* The CC function $f$ is $C^\infty$ by Lemma 3.1, and it was already noted above that $Df(t)$ is locally Lipschitz continuous, implying the uniform boundedness. For the coercivity, we expand $f$ into a Taylor series, $f(s + u') - f(s) = Df(s)u' + \mathcal{O}(\|u'\|^2_{\mathbb{V}})$. Inserting this into the strong monotonicity estimate (3.2), one obtains by choosing $u' = u/c$ small enough and then using linearity that

$$\langle Df(s)u, u\rangle \;\geq\; \gamma\;\|u\|^2_{\mathbb{V}} \;-\; \mathcal{O}(\|u\|^3_{\mathbb{V}}) \;\geq\; \gamma\|u\|^2_{\mathbb{V}} \;-\; \varepsilon$$

holds for all $u \in \mathbb{V}$ and $\varepsilon > 0$. This completes the proof.

□

**(ii) Proof of Theorem 3.2.** We start by proving an auxiliary lemma based on Lemma 2.5. It is the core ingredient to the proof of Theorem 3.2 performed thereafter.

**Lemma 3.4.** *Let $U_0 := span\{\Psi_0\}$. If the reference determinant $\Psi_0$ lies sufficiently close to the (intermediately normed) solution $\underline{\Psi}$ of the Schrödinger equation and $E^*$ is a simple eigenvalue of $H$, the restriction of the mapping $H - E^*$ to the orthogonal complement of $U_0$ is $\mathbb{H}^1$-elliptic, i.e.*

$$\langle \Psi, (H - E^*)\Psi \rangle \;\geq\; \gamma' \; \|\Psi\|^2 \tag{3.4}$$

*holds for some $\gamma' > 0$ and all $\Psi \in U_0^\perp$.*

*Proof.* We show that $H - E^*$ is elliptic on $U_0^\perp$ with respect to the $\mathbb{L}_2$-inner product $\langle \cdot, \cdot \rangle$ and then apply Lemma 2.5(ii). We let $\underline{P}, P_0$ be the $\mathbb{L}_2$-orthogonal projectors on $\mathrm{span}\{\underline{\Psi}\}$, $\mathrm{span}\{\Psi_0\}$, respectively, and denote the spectral gap by $\gamma^* := \inf(\mathrm{spec}(H)\backslash\{E^*\}) - E^*$ and the $\mathbb{L}_2$-norm by $|\cdot|$. Because $H - E^* = 0$ on $\mathrm{span}\{\underline{\Psi}\}$, there holds for any $\Psi \in U_0^\perp$ that

$$\langle \Psi, (H - E^*)\Psi \rangle \;=\; \langle (I - \underline{P})\Psi, (H - E^*)(I - \underline{P})\Psi \rangle \;\geq\; \gamma^* |(I - \underline{P})\Psi|^2$$

by use of the Courant-Fischer theorem [54]. We want to use $(I - P_0)\Psi = \Psi$, and compute the difference of the projectors: Letting $\bar{\underline{\Psi}} := \underline{\Psi}/|\underline{\Psi}|$, a short calculation shows that

$$\|P_0 - \underline{P}\|_{\mathbb{L}_2 \to \mathbb{L}_2} \;=\; \max_{f \in \mathbb{L}_2, |f|=1} \big|\, \langle f, \Psi_0 \rangle \Psi_0 - \langle f, \bar{\underline{\Psi}} \rangle \bar{\underline{\Psi}} \,\big| \;\leq\; |\Psi_0 - \bar{\underline{\Psi}}|. \tag{3.5}$$

Using orthogonality of $\Psi_0$ and $T\Psi_0$, there holds with $\tau = |T\Psi_0|, |\Psi_0| = 1$ that $\bar{\underline{\Psi}} = (\Psi_0 + T\Psi_0)/(1 + \tau^2)^{1/2}$, and one easily sees by orthogonal decomposition that

$$|\Psi_0 - \bar{\underline{\Psi}}|^2 = \big(1 - \frac{1}{(1-\tau^2)^{\frac{1}{2}}}\big)^2 + \frac{\tau^2}{(1-\tau^2)^{\frac{1}{2}}} \;=\; 2\big(\frac{1}{(1+\tau^2)} - \frac{1}{(1+\tau^2)^{\frac{1}{2}}}\big) \;=\; 4\tau^2 + \mathcal{O}(\tau^4).$$

Therefore, we can for instance choose $\tau = |\Psi_0 - \underline{\Psi}|$ such that $\|P_0 - \underline{P}\|_{\mathbb{L}_2 \to \mathbb{L}_2} \leq \frac{1}{2}$, and using $(I - P_0)\Psi = \Psi$ there follows

$$\gamma^* |(I - \underline{P})\Psi|^2 \;\geq\; \gamma^* \Big( \,|(I - P_0)\Psi| \;-\; |(P_0 - \underline{P})\Psi| \Big)^2 \;\geq\; \frac{1}{4}\, \gamma^* \; |\Psi|^2.$$

$H - E^*$ is thus $\mathbb{L}_2$-elliptic on the complement of $U_0$. Therefore – and because the Hamiltonian fulfils Gårding's inequality on $\mathbb{H}^1$, see (2.4) – Lemma 2.5 (ii) implies that there is a constant $\gamma'$ such that (3.4) holds for all $\Psi \in U_0^\perp$.

□

*Proof of Theorem 3.2 (Strong monotonicity of f).* To show (3.2), we denote the cluster operator belonging to $t^*$ by $T = \sum_{\alpha \in \mathcal{M}^*} t^*_\nu X_\nu$. We let $g_1 := s - t^*, g_2 := t - t^*$ and write the corresponding cluster operators as $G_1, G_2$. We expand $e^{G_i}, e^{-G_i}, i = 1, 2$ into a series to obtain

$$e^{-T-G_i}\hat{H}e^{T+G_i}\Psi_0 \;=\; e^{-T}\hat{H}e^{T}\Psi_0 \;-\; G_i e^{-T}\hat{H}e^{T}\Psi_0 \;+\; e^{-T}\hat{H}e^{T}G_i\Psi_0 \;+\; \mathcal{O}(\|g_i\|^2_{\mathbb{V}}).$$

Thus, with $G = G_1 - G_2$,

$$\begin{aligned}
\langle f(s) - f(t), s - t\rangle &= \langle f(t^* + g_1) - f(t^* + g_2), g_1 - g_2\rangle \\
&:= \langle G\Psi_0, e^{-T-G_1}He^{T+G_1}\Psi_0\rangle \;-\; \langle G\Psi_0, e^{-T-G_2}He^{T+G_2}\Psi_0\rangle \\
&\geq \langle G\Psi_0, e^{-T}He^{T}G\Psi_0\rangle \;-\; \langle G^\dagger G\Psi_0, e^{-T}He^{T}\Psi_0\rangle - \mathcal{O}(\|g_i\|^3_{\mathbb{V}}) \;=:\; (*)
\end{aligned}$$

by the Cauchy-Schwarz inequality and Theorem 2.4. Using $e^{-T}\hat{H}e^{T}\Psi_0 = E^*\Psi_0$, we have

$$\langle G^\dagger G\Psi_0, e^{-T}\hat{H}e^{T}\Psi_0\rangle = \langle G^\dagger G\Psi_0, E^*\Psi_0\rangle = E^*\langle G\Psi_0, G\Psi_0\rangle.$$

Thus, $(*)$ coincides up to second order with

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

and choosing an appropriate $\delta$ and $||g_1||_{\mathbb{V}}, ||g_2||_{\mathbb{V}} < \delta$, it suffices to show that this expression is bounded from below by $c \cdot \|g\|^2_{\mathbb{V}}$. We expand $e^T, e^{-T}$ into a power series as above to obtain

$$\begin{aligned}
&\langle G\Psi_0, e^{-T}(H - E^*)e^{T}G\Psi_0\rangle \\
=\;& \langle G\Psi_0, (H - E^*)G\Psi_0\rangle \;+\; \langle G\Psi_0, (H - E^*)(T - T^\dagger)G\Psi_0\rangle \;-\; \mathcal{O}(\|t^*\|^2_{\mathbb{V}}\|g\|^2_{\mathbb{V}}) \\
\geq\;& \gamma' \;\|G\Psi_0\|^2_{\mathbb{H}^1} \;-\; (\overline{\Lambda} - E^*)\;\|T - T^\dagger\|_{\mathbb{H}^1 \to \mathbb{H}^1}\|G\Psi_0\|^2_{\mathbb{H}^1} \;-\; \mathcal{O}(\|t^*\|^2_{\mathbb{V}}\|g\|^2_{\mathbb{V}})
\end{aligned}$$

where Lemma 3.4 was used in the last step, and the constant $\overline{\Lambda}$ stems from the upper bound (2.4) for the norm of $H$. Theorem 2.4 states that $\|T\|_{\mathbb{H}^1 \to \mathbb{H}^1}, \|T^\dagger\|_{\mathbb{H}^1 \to \mathbb{H}^1} \lesssim \|t^*\|_{\mathbb{V}}$, $\|G\Psi_0\|_{\mathbb{H}^1} \gtrsim \|g\|_{\mathbb{V}}$; if $\|t^*\|_{\mathbb{V}} \sim \|\Psi^*\|$ is small enough, this gives constants $c, \gamma'', \gamma > 0$ such that

$$\langle G\Psi_0, e^{-T}(\hat{H} - E^*)e^{T}G\Psi_0\rangle \quad\geq\quad \gamma''\|g\|^2_{\mathbb{V}} \;-\; c\|t^*\|_{\mathbb{V}}\|g\|^2_{\mathbb{V}} \;\geq\; \gamma\|g\|^2_{\mathbb{V}},$$

and the proof is finished.

## 4. Existence and uniqueness statements and error estimates

We now use the just proven properties of $f$ to obtain results about existence and (local) uniqueness for solutions of the problem (2.20) and for discretisations thereof. To this end, we recall at first how the discrete CC equations are embedded in the infinite dimensional context: In practice, one fixes a discrete one-particle basis $B_D$ for the formulation of a specific CC method (e.g. occupied orbitals from a discrete Hartree-Fock or DFT calculation, virtual orbitals orthogonal to the occupied ones), and thus the reference $\Psi_0$. From the corresponding Slater basis $\mathbb{B}_D$, a subset $\mathbb{B}_d$ is selected (e.g. singly and doubly excited Slater determinants for CCSD), corresponding to discrete coefficient spaces $\mathbb{V}_d \subseteq \mathbb{V}_D$, and the equations solved are the projected CC equations

$$\langle f(t_d), v_d \rangle \;=\; 0 \text{ for all } v_d \in \mathbb{V}_d. \tag{4.1}$$

The term "projected" herein refers to the fact that $B_d$ may for the theoretical purposes pursued here be complemented to a complete basis $B$, giving an according complete basis $\mathbb{B}$ of $\mathbb{H}^1$, so that (4.1) is indeed the Galerkin projection of the continuous CC equations (2.20), fixed by $\Psi_0$ and $\mathbb{B}$, on the subspace spanned by $\mathbb{B}_d$. This connection will be used to give statements on the solutions $t^*, t_d$ of the continuous and discretized equations in Part (i); also, we discuss the results. Part (ii) gives the proof of these results. In (iii), we derive estimates for the Coupled Cluster energy.

**(i) Existence and uniqueness of solutions; quasi-optimality of CC.** Note that our situation is a little different from what is usually assumed in the theory of standard nonlinear functional analysis [28, 65], where existence and uniqueness of continuous as well as discrete solutions follows if $f$ is globally Lipschitz continuous and globally strongly monotone (i.e. (3.2) holds on all of $\mathbb{V}$), see e.g. [26]. This cannot be true in our case if the eigenvalue problem (1.1) has a second solution, corresponding to a bound state aside from the ground state. Instead, existence of the solution of the continuous problem is in our case guaranteed by the Assumptions I-III together with Theorem 2.3, and we will prove the existence of local solutions of the corresponding discretised equations using some well-known results from operator analysis. Concerning uniqueness of continuous and discrete solutions, local statements are the best we can hope for if there are bound states aside from the ground state, and a result of that kind is given in the following theorem.

**Theorem 4.1.** *(Existence and uniqueness of solutions; quasi-optimality)*

*Let the assumptions of Theorem 3.2 be fulfilled. The Coupled Cluster function $f$ then possesses a Lipschitz continuous inverse $f^{-1}$ on $B_\delta(t^*)$; in particular, the solution $t^*$ of the Coupled Cluster function that belongs to the lowest eigenvalue of (1.1) is unique in the neighbourhood $B_\delta(t^*)$.*
*Let $\mathbb{V}_d$ be a subspace of $\mathbb{V}$ (corresponding to a subspace $\mathbb{H}^1_d$ of $\mathbb{H}^1$) for which*

$$d(t^*, \mathbb{V}_d) := \min_{v \in \mathbb{V}_d} \|v - t^*\|_{\mathbb{V}} = \min_{\Psi \in \mathbb{H}^1_d} \|\Psi - \Psi^*\|$$

*is sufficiently small. Then the discretised (projected) problem*

$$\langle f(t_d), v_d \rangle \;=\; 0 \text{ for all } v_d \in \mathbb{V}_d \tag{4.2}$$

*admits a solution $t_d$ in $B_{\delta,d} := \mathbb{V}_d \cap B_\delta(t^*)$ which is unique on $B_{\delta,d}$ and fulfils the quasi-optimality estimate*

$$\|t_d - t^*\|_{\mathbb{V}} \;\leq\; \frac{L}{\gamma}\, d(t^*, \mathbb{V}_d) \tag{4.3}$$

*with $L$ the Lipschitz constant and $\gamma$ the monotonicity constant of $f$ on $B_\delta(t^*)$. In particular, if $\mathbb{V}_{(n)}$ is a sequence of subspaces of $\mathbb{V}$ for which $\lim_{n\to\infty} d(t^*, \mathbb{V}_{(n)}) \to 0$, the corresponding solutions $t_{(n)} \in B_{\delta,(n)}$ of (4.2) converge to the continuous solution $t^* \in \mathbb{V}$.*

**Remarks.**

(i) Theorem 4.1 shows that if the monotonicity constant $\gamma$ is close to zero, which may happen due to a small gap between the ground state energy and the second lowest energy level of the Hamiltonian, or if one is faced with an unsufficient reference determinant, this may not only lead to deterioration of convergence of an e.g. Newton's method employed for solution of the Coupled Cluster equations as experienced in practice, but also means that the constants in the quasi-optimality estimate (4.3) become bad. Also, the results proven may in this case only hold on a very small neighbourhood of $t^*$, emphasing from another viewpoint the importance of multi-reference approaches in this situation.

(ii) The estimate (4.3) also shows that once a (possibly discrete) reference determinant is fixed, the quality of discrete solutions $t_d$ of the discrete CC method is exclusively determined by the choice of the subspace $\mathbb{H}^1_d$, that is, by the basis functions spanning the virtual space (the space orthogonal to span $B_{\text{occ}}$).

A question of particular interest is how the convergence of solutions of discrete CC equations towards the full solution of the electronic Schrödinger equation depends on the solution of the respective discrete Hartree-Fock/DFT equations on which the CC equations are based. The above result implies the following.

**Corollary 4.2.** *(Convergence of combined Hartree-Fock-CC calculations)*
*Let $(\Psi_{0,n})$ a sequence of reference determinants, build from a basis of invariant subspace of respective operators $F_n$ according to Assumption II, and $(\mathbb{B}_n)$ a sequence of according bases containing $\Psi_{0,n}$ respectively for all $n \in \mathbb{N}$. If uniformly for all $n \in \mathbb{N}$,*

(a) *the operators $F_n$ fulfil the spectral estimate (2.11) with constants $\lambda, \Lambda$,*
(b) *$\|\Psi_{0,n} - \underline{\Psi}\| \leq \epsilon$ holds uniformly, and if*
(c) *$d(\Psi^*, span\ \mathbb{B}_n) = d(t^*, \mathbb{V}_n) \ \leq \ \xi$ is sufficiently small,*

*the corresponding sequence of CC equations,*

$$f_n(t) \ = \ \langle \Psi_\alpha, e^{-T(t)} H e^{T(t)} \Psi_{0,n} \rangle \ = \ 0 \text{ for all } \Psi_\alpha \in \mathbb{B}_n$$

*for $f_n : \mathbb{V}_n \to \mathbb{V}_n'$ admits a sequence of solutions $t_n$ in $B_{\delta,n} := \mathbb{V}_n \cap B_\delta(t^*)$ which are unique on $B_{\delta,n}$ respectively, and which fulfil the uniform estimate*

$$\|t_d - t^*\|_{\mathbb{V}} \ \leq \ \frac{L}{\gamma}\, d(t^*, span\ \mathbb{B}_n). \tag{4.4}$$

*Proof.* The corollary follows from Theorem 4.1 together with the fact that once the constants $\lambda, \Lambda, \epsilon, \xi$ can be chosen uniformly, all estimates in this work hold uniformly (provided the Hamiltonian $H$ is fixed).

□

The above Corollary 4.2 assumes that the reference determinants $\Psi_{0,n}$ are close enough to the true solution $\underline{\Psi}$. Asymptotically, this is in particular the case if the sequence of reference determinants converges to a continuous limit $\Psi_{0,\text{cont}}$ fulfilling this condition; in the case of the canonical choice of the Fock operator for $F$, conditions (a) and (b) of the above Corollary 4.2 are then satisfied. Unfortunately, the convergence towards the continuous solution is an open question of Hartree-Fock theory. See [14] for a recent analysis of a related model problem.

**(ii) Proof of Theorem 4.1.** Equation (3.2) implies that $f$ is one-to-one on $B_\delta(t^*)$ and that for $p, q \in f(B_\delta(t^*))$, there holds for the inverse mapping $f^{-1} : f(B_\delta(t^*)) \to B_\delta(t^*)$

that

$$\gamma\|f^{-1}p - f^{-1}q\|^2 \;\leq\; \langle p-q,\; f^{-1}p - f^{-1}q\rangle \;\leq\; \|p-q\|\;\|f^{-1}p - f^{-1}q\|,$$

so $f^{-1}$ is Lipschitz continuous with Lipschitz constant $1/\gamma$. To prove the existence of solutions for sufficiently well discretised problems, we use the following well-known lemma which bases on the fixed point theorem of Brouwder, see e.g. [26], Lemma 4.2.1 for a proof.

**Lemma 4.3.** *Let $\|.\|_\#$ be an arbitrary norm on $\mathbb{R}^m$, and $\mathbf{h} : \mathbb{R}^m \to \mathbb{R}^m$ be a continuous function on the closed ball $\overline{B}_{R,\|.\|_\#}(\mathbf{0})$ of radius $R$ around $\mathbf{0} \in \mathbb{R}^m$. If $\langle \mathbf{h}(\mathbf{v}), \mathbf{v}\rangle \geq 0$ holds for all $\mathbf{v} \in \mathbb{R}^m$ with $\|\mathbf{v}\|_\# = R$, there is a $\mathbf{v}^* \in \overline{B}_{R,\|.\|_\#}(\mathbf{0})$ for which $\mathbf{h}(\mathbf{v}^*) = \mathbf{0}$.*

To finish the proof of Theorem 4.1, let us now fix a discretisation $\mathbb{V}_d \subseteq \mathbb{V}$ for which $d := d(t^*, \mathbb{V}_d) \leq \delta \cdot \gamma/(\gamma + L)$. We let $m := \dim \mathbb{V}_d$, $\mathbb{B}_d := \{b_j \in \mathbb{V}, j \in m\rfloor\}$ be an orthonormal basis of $\mathbb{V}_d$ and $t^{\rm opt} = \arg\min d(t^*, \mathbb{V}_d)$.[2] To apply Lemma 4.3, we define for $\mathbf{v} = (v_j)_{j=1}^m \in \mathbb{R}^m$ that $v = \sum_{j=1}^m v_j b_j$ and $\|\mathbf{v}\|_\# := \|v\|_{\mathbb{V}}$. We let

$$\mathbf{h}(\mathbf{v}) \;=\; \big(\langle f(t^{\rm opt} + \sum_{j=1}^m v_j\varphi_j),\; \varphi_k\rangle\big)_{k=1}^m$$

and observe that $\mathbf{h}(\mathbf{v}) = \mathbf{0}$ for some $\mathbf{v} \in \overline{B}_{R,\#}(\mathbf{0})$ iff $t^{\rm opt} + \sum_{j=1}^m v_j b_j \in \overline{B}_{R,\mathbb{V}}(t^{\rm opt})$ solves the discretised problem (4.2). Choosing $R = \delta - d$, $\overline{B}_{R,\mathbb{V}}(t^{\rm opt})$ lies in the neighbourhood of $t^*$ where $f$ is strongly monotone, so for all $\mathbf{v} \in \mathbb{R}^m$ with $\|\mathbf{v}\|_\# = R$,

$$\begin{aligned}
\langle \mathbf{h}(\mathbf{v}), \mathbf{v}\rangle \;&:=\; \langle f(t^{\rm opt} + v), v\rangle \\
&=\; \langle f(t^{\rm opt} + v) - f(t^{\rm opt}), v\rangle \;+\; \langle f(t^{\rm opt}) - f(t^*), v\rangle \\
&\geq\; \gamma\|\mathbf{v}\|_\#^2 - Ld\|\mathbf{v}\|_\# \;=\; R(\gamma R - Ld) \;\geq\; 0,
\end{aligned}$$

and because of the local Lipschitz continuity of $f$, $\mathbf{h}$ is continuous on $\overline{B}_R(0)$. Thus, $\mathbf{h}$ fulfils the conditions of Lemma 4.3, and if $\mathbf{v}^* = (v_j^*)_{j=1}^m \in \overline{B}_{R,\#}(\mathbf{0})$ solves $\mathbf{h}(\mathbf{v}^*) = \mathbf{0}$, then $t_d := t^{\rm opt} + \sum_{j=1}^m b_j^*\varphi_j \in \overline{B}_{R,\mathbb{V}}(t^{\rm opt}) \subseteq B_\delta(t^*)$ is a solution of (4.2). The restriction $\tilde{f} : B_{d,\delta}(t^*) \to \mathbb{V}_d'$ of $f$ is also a strongly monotone function, so that with the same argumentation as for the continuous solution, there can only be one $t_d \in B_{d,\delta}(t^*)$ solving $\tilde{f}(t_d) = 0 \in \mathbb{V}_d'$, proving local uniqueness of the solution. The quasi-optimality estimate and the convergence of the discrete solutions $t_d$ towards the continuous limit $t^*$ now follow from Lipschitz continuity and strong monotonicity of $f$ by standard arguments, see e.g. [65].

[2] Note that $\mathbb{V}$ is a Hilbert space, see the remarks after (2.16).

□

**(iii) Error estimates for the Coupled Cluster energy.** To end this section, we now combine the results just proven with the formalism of goal oriented error estimators developed in [9] and also used in [58] to obtain estimators for the Coupled Cluster energy (2.19),

$$E(t) = \langle \Psi_0, e^{-T(t)} \hat{H} e^{T(t)} \Psi_0 \rangle, \tag{4.5}$$

in terms of the approximation quality of the cluster amplitudes $(t_\alpha)_{\alpha \in \mathcal{M}^*}$ and the corresponding wave functions. To do so, we use that the ground state energy $E^*$ is a minimizer of a corresponding Lagrange functional. Because this Lagrangian is non-symmetric, we cannot expect the error to be quadratic with respect to the error of the wave function as for the energies obtained e.g. by Hartree-Fock or CI calculations. Instead, the solution $z^*$ of the *dual problem* (corresponding to the Lagrangian multipliers in the finite-dimensional setting) enters the estimates, and we introduce the necessary terminology in the next lemma.

**Lemma 4.4.** *(Properties of dual solutions)*

*Let $\mathbb{V}_d$ be a sufficiently good subspace of $\mathbb{V}$, and $t^* \in \mathbb{V}$ and $t_d \in \mathbb{V}_d$ solutions the Coupled Cluster equations (2.19) and of the discretised (projected) Coupled Cluster equations respectively,*

$$\langle f(t^*), s \rangle = 0 \quad \textit{for all} \quad s \in \mathbb{V}, \qquad \langle f(t_d), s_d \rangle = 0 \quad \textit{for all} \quad s_d \in \mathbb{V}_d. \tag{4.6}$$

*Under the assumptions of Theorem 3.2, there is a unique "dual solution" or "Lagrangian multiplier" $z^* \in \mathbb{V}$ determined by $t^*$ such that $(t^*, z^*)$ is a stationary point of the Lagrangian $\mathcal{L}(t, z) = E(t) + \langle f(t), z \rangle$ , i.e. $(t^*, z^*)$ solves*

$$\mathcal{L}'(t^*, z^*) = \left\{ \begin{array}{c} \langle E'(t^*), s \rangle - \langle Df(t^*)s, z^* \rangle \\ \langle f(t^*), s \rangle \end{array} \right\} = 0 \qquad \textit{for all } s \in \mathbb{V}. \tag{4.7}$$

*For a sufficiently good discretisation $\mathbb{V}_d$, there is a corresponding unique $z_d \in \mathbb{V}$ such that $(t_d, z_d)$ solves the discretised equations*

$$\mathcal{L}'(t_d, z_d) = \left\{ \begin{array}{c} \langle E'(t_d), s_d \rangle - \langle Df(t_d)s_d, z_d \rangle \\ \langle f(t_d), s_d \rangle \end{array} \right\} = 0 \qquad \textit{for all } s_d \in \mathbb{V}_d \tag{4.8}$$

*The discrete dual solution $z_d$ approximates the exact dual solution quasi-optimally in the sense that*

$$\|z_d - z^*\|_{\mathbb{V}} \lesssim \Delta := \max\{d(\mathbb{V}_d, t^*),\ d(\mathbb{V}_d, z^*)\}. \tag{4.9}$$

*Proof.* By definition, $t^*$ solves the second equation from (4.7), so we only have to show that the first equation $\langle E'(t^*), s\rangle = \langle Df(t^*)s, z^*\rangle$ admits a unique solution $z^*$. Indeed, this is an equation for the linear operator $Df(t^*)^\dagger : \mathbb{V} \to \mathbb{V}'$, which is bounded and coercive because its adjoint $Df(t^*)$ is by Corollary 3.3. Therefore, the Lax-Milgram theorem (see e.g. [3]) ensures existence and uniqueness of $z^*$. The same argument holds for $z_d$ if the discretisation is fine enough to guarantee (together with quasi-optimality of $t_d$) that $Df(t_d)$ is also coercive, cf. Corollary 3.3. To show (4.9), we decompose $z_d - z^* = z_d - \hat{z}_d + \hat{z}_d - z^*$, where $\hat{z}_d \in \mathbb{V}_d$ solves the discrete system

$$\langle E'(t^*), s_d\rangle = \langle Df(t^*)s_d, \hat{z}_d\rangle \quad \text{for all} \quad s_d \in \mathbb{V}_d. \tag{4.10}$$

Because $Df(t^*)$ is a bounded and coercive linear mapping, see Corollary 3.3, $\hat{z}_d$ approximates the solution $z^*$ of the corresponding continuous problem (4.7) quasi-optimally by Cea's lemma [3], $\|\hat{z}_d - z^*\|_{\mathbb{V}} \lesssim d(\mathbb{V}_d, z^*)$. For $\|z_d - \hat{z}\|_{\mathbb{V}}$, we at first note again that $Df(t)$ and also by very similar arguments the derivative $E'(t)$ of the energy expression (4.5) are Lipschitz continuous on bounded neighbourhoods of $t^*$. We choose $c > 0$ such that by Theorem 4.1, for a each discretisation $\mathbb{V}_d$ for which $d(t^*, \mathbb{V}_d) < c$ there holds $\|t_d - t^*\|_{\mathbb{V}} \leq L/\gamma\ d(t^*, \mathbb{V}_d)$ for the discrete solution $t_d$, and let $L_{f'}$ and $L_{E'}$ be the Lipschitz constants of $Df(t)$ and $E'(t)$ on $B_{cL/\gamma}(t^*)$. We now obtain using (4.8), (4.10) that

$$\begin{aligned}
\gamma\|z_d - \hat{z}_d\|_{\mathbb{V}}^2 &\leq \langle Df(t_d)(z_d - \hat{z}_d), z_d - \hat{z}_d\rangle \\
&= \langle E'(t_d) - E'(t^*), (z_d - \hat{z}_d)\rangle + \langle (Df(t^*) - Df(t_d))(z_d - \hat{z}_d), \hat{z}_d\rangle \\
&\leq (L_{E'} + L_{f'}\|\hat{z}\|_{\mathbb{V}})\ \|t_d - t^*\|_{\mathbb{V}}\ \|z_d - \hat{z}_d\|_{\mathbb{V}},
\end{aligned}$$

and observe that $\|\hat{z}\|_{\mathbb{V}}$ is bounded by $\|z^*\|_{\mathbb{V}} + c \cdot d(\mathbb{V}_d, z^*)$, so that

$$\|z_d - \hat{z}_d\|_{\mathbb{V}} \lesssim \|t_d - t^*\|_{\mathbb{V}} \lesssim d(\mathbb{V}_d, t^*).$$

Thus, $\|z_d - z^*\|_{\mathbb{V}} \lesssim \Delta$, finishing the proof.

□

The quality of a discrete solution $(t_d, z_d)$ of the above Lagrangian equations can be measured in terms of the primal residual $\rho(t_d)$ and the dual residual $\rho^*(t_d, z_d)$, given by

$$\rho(t_d) \;:=\; \langle f(t_d), \cdot\rangle_{\mathbb{V}} \qquad \rho^*(t_d, z_d) \;:=\; \langle E'(t_d), \cdot\rangle_{\mathbb{V}} - \langle Df(t_d)\cdot, z_d\rangle_{\mathbb{V}} \tag{4.11}$$

The theory developed in [5, 9] now allows to estimate the error of the energy approximation in terms of these primal and dual residuals. We first adapt the original theorem from [5] to our notation in (i) and then derive some quasi-optimality estimates for the Coupled Cluster method in (ii), (iii). The estimates again hold uniformly for different CC functions based on different reference determinants $\Psi_0$ and bases $\mathbb{B}$ if the conditions given in Corollary 4.2 are satisfied.

**Theorem 4.5.** *(Energy estimators)*

(i) *(Becker/Rannacher [9], see [5] Proposition 6.2.)*

*Let $(t^*, z^*) \in \mathbb{V}^2$ and $(t_d, z_d) \in \mathbb{V}_d^2$ be the solutions of minimization problems (4.7), (4.8) for a thrice differentiable functional $\mathcal{L}$. Then there holds*

$$E(t^*) - E(t_d) \;=\; \frac{1}{2}\rho(t_d)(z^* - v_d) \;+\; \frac{1}{2}\rho^*(t_d, z_d)(t^* - w_d) \;+\; \mathcal{R}_d^3 \tag{4.12}$$

*for all $v_d, w_d$ in $\mathbb{V}_d$, where*

$$\mathcal{R}_d^3 = \mathcal{O}(\max\{\|t^* - t_d\|, \|z^* - z_d\|\}^3)$$

*depends cubically on the primal and dual errors.*

(ii) *Let $\mathbb{V}_d$ be a sufficiently large subspace of $\mathbb{V}$ in the sense that for $\Delta$ from (4.9), $\Delta < c$ for a suitable $c > 0$, and denote by $(t^*, z^*)$ and $(t_d, z_d)$ the solutions the Coupled Cluster equations and of the discretised (projected) Coupled Cluster equations (4.6), respectively, together with the corresponding unique dual solutions. Under the assumptions of Theorem 3.2, there holds*

$$|E(t^*) - E(t_d)| \;\leq\; \|t_d - t^*\|_{\mathbb{V}} \left(c_1 \,\|t_d - t^*\|_{\mathbb{V}} \;+\; c_2 \,\|z_d - z^*\|_{\mathbb{V}}\right),$$

$$|E(t^*) - E(t_d)| \;\lesssim\; \left(\, d(\mathbb{V}_d, t^*) \;+\; d(\mathbb{V}_d, z^*) \,\right)^2.$$

*where the above constants are specified in the proof.*

(iii) *Denoting $\underline{\Psi}^{z^*} := \Psi_0 + \Psi^{z^*} := e^{T(z^*)}\Psi_0$, by $\underline{\Psi} = \Psi_0 + \Psi^*$ the solution of the exact eigenproblem (1.1) and by $\mathbb{H}^1_{d,\perp}$ the discretisation of $(\mathrm{span}\{\Psi_0\})^\perp$ corresponding*

*to $\mathbb{V}_d$, there holds*

$$|E(t^*) - E(t_d)| \lesssim \| e^{T(t_d)}\Psi_0 - \underline{\Psi}\| \cdot \big( \| e^{T(t_d)}\Psi_0 - \underline{\Psi}\|^2 + \| e^{T(z_d)}\Psi_0 - \underline{\Psi}^{z^*}\| \big),$$

$$|E(t^*) - E(t_d)| \lesssim \Big( \inf_{\Psi\in\mathbb{H}^1_{d,\perp}} \|\Psi - \Psi^*\| + \inf_{\Psi\in\mathbb{H}^1_{d,\perp}} \|\Psi - \Psi^{z^*}\| \Big)^2.$$

*Proof.* For the proof of (i), cf. [5]. To prove (ii), we choose $\tilde{c} > 0$ such that for a each discretisation $\mathbb{V}_d$ for which $d(t^*, \mathbb{V}_d) < \tilde{c}$, there holds $\|t_d - t^*\|_{\mathbb{V}} \leq L/\gamma\ d(t^*, \mathbb{V}_d)$ for the discrete solution $t_d$ by Theorem 4.1. We denote by $L$, $L_{f'}$ and $L_{E'}$ the Lipschitz constants of $f(t)$, $Df(t)$ and $E'(t)$ on $B_{\tilde{c}L/\gamma}(t^*)$, and note that by Corollary 3.3, $\|Df(t)\|_{\mathbb{V}\to\mathbb{V}'}$ is uniformly bounded by a constant $C$ on $B_{\tilde{c}L/\gamma}(t^*)$. We now use (4.7) to rewrite the dual residual by inserting zeros as

$$\rho^*(t_d, z_d)(s) = \langle E'(t_d) - E'(t^*), s\rangle_{\mathbb{V}} + \langle \big(Df(t^*) - Df(t_d)\big)s, z^*\rangle_{\mathbb{V}} + \langle Df(t_d)s, z^* - z_d\rangle_{\mathbb{V}}$$

for arbitrary $s \in \mathbb{V}$. Thus, with (4.12) and the definition of the primal residual $\rho(t_d)$, we obtain that for all $v_d, w_d$ in $\mathbb{V}_d$, there holds according to (i) that

$$\begin{aligned}
& 2|E(t^*) - E(t_d)| \\
\leq\ & |\langle f(t_d) - f(t^*), z^* - v_d\rangle_{\mathbb{V}}| + |\langle E'(t_d) - E'(t^*), t^* - w_d\rangle_{\mathbb{V}}| \\
& + |\ \langle \big(Df(t^*) - Df(t_d)\big)(t^* - w_d), z^*\rangle_{\mathbb{V}}\ | + |\langle Df(t_d)(t^* - w_d), z^* - z_d\rangle_{\mathbb{V}}| + 2\mathcal{R}_d^3 \\
\leq\ & L\|t_d - t^*\|_{\mathbb{V}}\|z^* - v_d\|_{\mathbb{V}} + L_{E'}\|t_d - t^*\|_{\mathbb{V}}\|t^* - w_d\|_{\mathbb{V}} \\
& + L_{f'}\|t^* - t_d\|_{\mathbb{V}}\|t^* - w_d\|_{\mathbb{V}}\|z^*\|_{\mathbb{V}} + C\ \|t^* - w_d\|_{\mathbb{V}}\|z^* - z_d\|_{\mathbb{V}} + 2\mathcal{R}_d^3 := (*).
\end{aligned}$$

Inserting $v_d = t_d, w_d = z_d$, we obtain

$$\begin{aligned}
|E(t^*) - E(t_d)| &\leq \frac{1}{2}\|t_d - t^*\|_{\mathbb{V}} \Big( (L_{f'}\|z^*\|_{\mathbb{V}} + L_{E'})\ \|t_d - t^*\|_{\mathbb{V}} + (L + C)\ \|z_d - z^*\|_{\mathbb{V}} \Big) + \mathcal{R}_d^3 \\
&=: \|t_d - t^*\|_{\mathbb{V}} \Big( c_1\ \|t_d - t^*\|_{\mathbb{V}} + c_2\ \|z_d - z^*\|_{\mathbb{V}} \Big) + \mathcal{R}_d^3.
\end{aligned}$$

By Lemma 4.4, $\|z_d - z^*\|_{\mathbb{V}}$ is bounded by $\Delta$; thus, we can (by additionally using the quasi-optimality of $t_d$, Theorem 4.1) control the remainder term $\mathcal{R}_d^3$ in terms of $\mathcal{O}(\Delta^3)$. Therefore, the first estimate of (ii) is proven by choosing $\Delta$ small enough, while the second follows from $(*)$ by inserting for $v_d, w_d$ the best approximations $t^{\mathrm{opt}}, z^{\mathrm{opt}} \in \mathbb{V}_d$ of $t^*, z^*$. To prove (iii), we utilize Theorem 2.4(ii): The first estimate follows from the first one of (ii) with the observation that locally,

$$\|t - s\|_{\mathbb{V}} = \|T(t)\Psi_0 - T(s)\Psi_0\|_F \sim \|e^{T(t)}\Psi_0 - e^{T(s)}\Psi_0\|_F$$

holds; for the second, we use that $\{\exp(T(t)) \mid t \in \mathbb{V}_d\} = \{I + T(t) | t \in \mathbb{V}_d\}$, cf. Theorem 2.4(ii), together with the second estimate given in (ii).

□

## 5. Concluding remarks

In this paper, we used the infinite dimensional, continuous formulation of the Coupled Cluster method derived in [56] to apply to it concepts of nonlinear operator theory along the lines of [58], and this ansatz has enabled us to formulate direct error estimates with respect to the continuous solution $\Psi$. In particular, the equations obey similar estimates as the corresponding full-CI-equations, with the Galerkin-typical quadratic dependence of the eigenvalues on the error of the iterates replaced by the nonvariational dual estimate from (4.5). These estimates provide a tool that might be used for error estimation with an appropriate refinement strategy, for instance by using hierarchical basis sets as the VnZ-bases used in extrapolation schemes, or also by selecting subsets of a discretised set of amplitudes to estimate the effect of including e.g. only some of the $T_2$ amplitudes in a classical CCSD calculation.

Our analysis also displays the importance of the spectral gap (3.4) and of the quality of the reference determinant not only for the convergence of the method, but also for the constants in optimality estimates. If these quantities are well-behaved, the proof of Theorem (3.2) shows that the CC function can then be viewed as a small perturbation of the symmetric operator $(H - E^*)$. Continuity arguments imply in this case that primal and dual solution do not differ much, so that if $d(z^*, \mathbb{V}_d) \lesssim d(t^*, \mathbb{V}_d)$ holds, the CC energy converges quadraticly with the error in $t^*$ – a behaviour that may often be observed in practice for well-behaved examples. On the other hand, our analysis also underlines the general weakness of the practical Coupled Cluster method if the spectral gap (3.4) is too small or if multiple eigenvalues occur, or if the reference determinant $\Psi_0$ is of poor quality. In this case, multireference methods [11, 49, 52] have to be utilized, and it would be desirable to use the theoretical framework developed here to attack this problem and also the approaches of time dependent CC and variational CC (see e.g. [38] and references therein) from the viewpoint of numerical analysis in the near future.

## Appendix A. Practical aspects of the CC method

In this final supplementary section, we want to give a brief overview on how the continuous CC equations (2.19) resp. their projected versions (2.22) are treated in practice. As a first step towards implementation, the CC equations are simplified by rewriting the term $e^{-T(t)}He^{T(t)}$ by means of the Baker-Campbell-Haussdorff formula, giving a series expansion which terminated at fourth order due to the structure of the Hamiltonian. Here, we will give a short and to the author's mind more transparent proof of this fact than the canonical one that can e.g. be found in [30]; the according expression for the similarity transformed Hamiltonian $e^{-T}He^{T}$ (with $T = T(t)$, also covering the continuous case) will be given in part (i), Theorem A.1, while using the formalism of second quantization, the main part of the proof is performed in (ii) and (iii). Afterwards, we will for sake of brevity only make some remarks about how the resulting terms are evaluated in practice in (iv) and refer the reader to the literature for further reference. In particular, we will not try to compete with the vast amount of practical experience made with the CC method in the field of quantum chemistry; for numerical examples for the performance of the CC method, we therefore refer [30] and the references given therein. The section will be ended in part (v) by a uniform convergence estimate for Newton's method applied to the CC equations, which we trivially obtain from the strong monotonicity results for $f$.

**(i) Formulation of CC in terms of annihilation and creation operators.** We already mentioned above that the projected Coupled Cluster equations (i.e. the term $e^{-T}He^{T}$) can be evaluated exactly within arithmetic precision. This is due to the fact that in the linked Coupled Cluster equations (2.19), the term $e^{-T}He^{T}$ can be expanded into the so-called Baker-Campbell-Hausdorff series, which itself terminates because the Hamiltonian is a two-particle operator [30]. To state the result precisely, we define for any operator $A : H^1 \to H^{-1}$ the (iterated) commutators $[A,T]_{(0)} := A$, $[A,T]_{(1)} := AT - TA : H^1 \to H^{-1}$ and $[A,T]_{(n)} := [[A,T]_{(n-1)},T]$ for $n \geq 2$, and note that these expressions are well-defined due to Theorem 2.4.

**Theorem A.1.** *(Evaluation of the similarity transformed Hamiltonian $e^{-T}He^{T}$)*
*For the Hamiltonian $H : \mathbb{H}^1 \to \mathbb{H}^{-1}$, there holds*

$$e^{-T}He^{T} \;=\; \sum_{n=0}^{4} \frac{1}{n!}[H,T]_{(n)}. \tag{A.1}$$

The first part of the proof is the below globalization of the Baker-Campbell-Hausdorff series expansion (as canonically formulated for matrices). Afterwards, we show in (ii), (iii) that the iterated commutators $[H,T]_{(n)}$ give zero contributions for $n > 4$.

**Lemma A.2.** *For any operator $A : H^1 \to H^{-1}$, there holds the* Baker-Campbell-Hausdorff formula,

$$e^{-T} A e^{T} \;=\; \sum_{n=0}^{\infty} \frac{1}{n!} [A,T]_{(n)}. \tag{A.2}$$

*Proof.* It is not hard to show by induction that $[A,T]_{(n)} = \sum_{i=0}^{n} \binom{n}{i} (-1)^i T^i A T^{n-i}$. Thus,

$$e^{-T} A e^{T} \;=\; \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{(-T)^i}{i!} A \frac{T^j}{j!} \;=\; \sum_{n=0}^{\infty} \sum_{i=0}^{n} (-1)^i \frac{T^i}{i!} A \frac{T^{n-i}}{(n-i)!} \;=\; \sum_{n=0}^{\infty} \frac{1}{n!} [A,T]_{(n)}.$$

□

**(ii) The CC equations in Second Quantization.** The fact that the Baker-Campbell-Hausdorff series terminates can be best understood in terms of annihilation and creation operators borrowed the formalism of Second Quantization. We therefore quickly repeat some facts from [56], where we globalized the canonical definition via a finite-dimensional basis [30,61] to the full space $\mathbb{L}$. For a more detailed treatment, see the afore mentioned references. At the end of the present part (ii), we obtain an expression for the similarity transformed Hamiltonian $e^{-T} H e^{T}$ in terms of annihilation and creation operators.

We start by defining the (fermion) Fock space [27] as

$$\mathbb{F} \;:=\; \bigoplus_{i=0}^{\infty} \mathbb{L}^2_i,$$

where $\bigoplus$ denotes the direct orthogonal sum, and $\mathbb{L}^2_i := L^2((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^i)$ denotes the $i$-electron state space. In particular, $\mathbb{L}^2 = \mathbb{L}^2_N$ is embedded in $\mathbb{F}$. As before, we fix a one-particle basis $B = \{\chi_P | P \in \mathcal{I}\}$. For each $\chi_P \in B$, we define a corresponding *creation operator* $a^\dagger_P$ on the Fock space $\mathbf{F}$: We fix its action on an $i$-electron Slater determinant $\Psi_{\mu,i} \in \mathbb{B}_i$ as

$$a^\dagger_P \Psi_{\mu,i} \quad := \quad \mathcal{Q}_{i+1}\big(\chi_P \otimes \Psi_{\mu,i}\big). \tag{A.3}$$

with the antisymmetrization mapping $\mathcal{Q}_{i+1} : L^2\big((\mathbb{R}^3 \times \{\pm\frac{1}{2}\}^{N+1}\big) \to \mathbb{L}^2_{N+1}$ defined analogously to $\mathcal{Q}_N$ from (2.8). For $N = 0$, we let $a^\dagger_P |\rangle \;=\; \chi_P \in \mathbb{L}^2_1$. By linear continuation and

closing the operator in $\mathbb{F}$, we obtain a bounded operator defined on all of $\mathbb{F}$, that adds to any $i$-electron Slater determinant $\Psi_{\mu,i}$ the basis function $\chi_P$ to obtain an antisymmetric $i+1$-electron Slater determinant; if $\chi_P$ is contained in $\Psi_{\mu,i}$, the action of $\mathcal{Q}_{i+1}$ results in $a_P^\dagger \Psi_{\mu,i} = 0$.
The corresponding *annihilation operator* $a_P : \mathbb{F} \to \mathbb{F}$ of $\chi_P$ is defined as the adjoint of $a_P^\dagger : \mathbb{F} \to \mathbb{F}$; it "removes" $\chi_P$ from the Slater determinant $\Psi_{\mu,i}$, or returns $a_P^\dagger \Psi_{\mu,i} = 0$ if $\chi_P$ is not contained in $\Psi_{\mu,i}$.

Among many other properties [30,61] of annihilation and creation operators, the probably most important are the rules for computation of their anticommutators $[A,B]_+ := AB + BA$,

$$[a_P, a_Q]_+ = 0, \qquad [a_P^\dagger, a_Q^\dagger]_+ = 0, \qquad [a_P, a_Q^\dagger]_+ = [a_P^\dagger, a_Q]_+ = \delta_{P,Q} \tag{A.4}$$

for all $P, Q \in \mathcal{I}$, where $\delta_{P,Q} = 1$ only if $P = Q$ and $\delta_{P,Q} = 0$ otherwise, and we will now use these properties to simplify the expression $e^{-T} H e^T$ turning up in the CC equations. We therefore use that the Hamiltonian $H$ can be expressed [55] in Second Quantization form as

$$H \;=\; \sum_{P,Q \in \mathcal{I}} h_{PQ} a_P^\dagger a_Q \;+\; \sum_{P,Q,R,S \in \mathcal{I}} \langle PQ||RS\rangle a_P^\dagger a_Q^\dagger a_S a_R. \tag{A.5}$$

with the *single electron interaction integrals*

$$h_{PQ} \;:=\; \frac{1}{2}\langle \nabla\chi_P, \nabla\chi_Q\rangle + \sum_{\nu=1}^{K} \langle \chi_P, \frac{Z_\nu}{|x_i - R_\nu|}\chi_Q\rangle \tag{A.6}$$

and the *electron pair interaction integrals*

$$\langle PQ|RS\rangle \;:=\; \sum_{s,s' \in \{\pm\frac{1}{2}\}} \int_{\mathbb{R}^6} \chi_P(x,s)\chi_Q(y,s') \frac{1}{|x-y|} \chi_R(x,s)\chi_S(y,s')\, dxdy \tag{A.7}$$

defining the *antisymmetrized integrals*

$$\langle PQ||RS\rangle \;:=\; \frac{1}{2}\Big(\langle PQ|RS\rangle - \langle PQ|SR\rangle\Big). \tag{A.8}$$

Next, we rewrite cluster operators $T = \sum_{\mu \in \mathcal{M}} t_\mu X_\mu$ in terms of creation and annihilation operators: We start by noting that for any given $\mu \in \mathcal{M}^*$ the corresponding determinant $\Psi_\mu$ can be obtained from $\Psi_0$ by exchanging $r$ indices $I_1 < \ldots < I_r \in \text{occ}$ against virtual indices $A_1 < \ldots < A_r \in \text{virt}$. It is then not hard to check that any excitation operator $X_\mu$

as fixed in Definition 2.2 can be expressed in terms of annihilation and creation operators as

$$X_\mu = X^{A_1,\ldots,A_r}_{I_1,\ldots,I_r} = a^\dagger_{A_1} \ldots a^\dagger_{A_r} a_{I_1} \ldots a_{I_r} \tag{A.9}$$

with $I_1 < \ldots < I_r \in \text{occ}$, $A_1 < \ldots < A_r \in \text{virt}$. Thus, the central part $e^{-T} H e^T$ can be expressed completely in terms of annihilation and creation operators.

**(iii) Termination of the Baker-Campbell-Hausdorff series.** The key to prove the missing part of Theorem A.1 is the below Lemma A.3. Before it can be formulated, we need one notation: Let $\mathcal{E}$ be an arbitrary set of annihilation and creation operators, $B = b_1 \ldots b_n$ an *operator string*, i.e. an operator built of annihilation and creation operators. We denote by

$$\mathcal{C}_\mathcal{E}(B) = \left| \left\{ b_i \mid i \in N\rfloor \,,\ \exists\, e \ \in\ \mathcal{E} \text{ such that } [b_i, e]_+ \neq 0 \right\} \right|$$

the number of operators in $B$ that do not anticommute with all contained in $\mathcal{E}$.

**Lemma A.3.** *Let $\mathcal{E}$ be an anticommuting set of annihilation operators, $[e, f]_+ = 0$ for all $e, f \in \mathcal{E}$, and $B, C$ be operator strings for which $B = b_1 \ldots b_{2n}$ contains an even number of operators and for which for $C = c_1 \ldots c_m, c_i \in \mathcal{E}$ for all $i \in m\rfloor$. Then, if $\mathcal{C}_\mathcal{E}(B) = 0$, there holds $[B, C] = 0$, and in case $\mathcal{C}_\mathcal{E}(B) \geq 1$, we can write $[B, C] = \sum_{i=1}^n B_i$ with operator strings $B_i$ for which $\mathcal{C}_\mathcal{E}(B_i) \leq \mathcal{C}_\mathcal{E}(B) - 1$.*

*Proof.* We proceed by induction over $m$. For $m = 1$, there follows by definition of the anticommutator that by swapping $c_1$ to the left,

$$\begin{aligned} [B, c_1] &= b_1 \ldots b_{2n} c_1 \ - \ c_1 b_1 \ldots b_{2n} \\ &= (-1)^{2n} c_1 b_1 \ldots b_{2n} \ - \ c_1 b_1 \ldots b_{2n} + \sum_{i=0}^{2n} (-1)^i [b_i, c_1]_+ \ b_1 \ldots b_{i-1} b_{i+1} \ldots b_{2n}. \end{aligned}$$

The first two terms cancel. In the sum in the last, we have in each summand either $[b_i, c_1]_+ = 0$, or that $[b_i, c_1]_+ = 1$ and the operator string $b_1 \ldots b_{i-1} b_{i+1} \ldots b_{2n}$ contains one operator less not anticommuting with all operators from $C$. Thus, if $\mathcal{C}_\mathcal{E}(B) = 0$, we have $[b_i, c_1]_+ = 0$ for all $1 \leq i \leq N$, so $[B, c_1] = 0$, and if $\mathcal{C}_\mathcal{E}(B) \geq 1$, $[B, C]$ is a sum of operator strings $B_i$ for which $\mathcal{C}_\mathcal{E}(B_i) \leq \mathcal{C}_\mathcal{E}(B) - 1$. For the induction step, we use the

same proceeding for $C = c_1 \dots c_{m+1}$ to swap $c_{m+1}$ to the right,

$$\begin{aligned}[B,C] &= b_1 \dots b_{2n} c_1 \dots c_{m+1} - c_1 \dots c_m c_{m+1} b_1 \dots b_{2n} \\ &= [B,C_m]c_{m+1} + \sum_{i=0}^{2n} (-1)^i [c_{m+1}, b_i]_+ \; c_1 \dots c_m b_1 \dots b_{i-1} b_{i+1} \dots b_{2n},\end{aligned}$$

where we let $C_m = c_1 \dots c_m$. In the case that $\mathcal{C}_\mathcal{E}(B) = 0$, there follows $[B, C_m]c_{m+1} = 0$ by induction hypothesis, and all summands in the second term are also zero because $[c_{m+1}, b_i]_+ = 0$. Thus, $[B,C] = 0$. If $\mathcal{C}_\mathcal{E}(B) \neq 0$, we observe for the left term that by induction hypothesis, we can write $[B, C_m]$ as a sum of operator strings $B_i$ for which $\mathcal{C}_\mathcal{E}(B_i) \leq \mathcal{C}_\mathcal{E}(B) - 1$, so the same holds for $[B, C_m]c_{m+1}$. For the right term, the same argument as in the case $m = 1$ gives that each summand can only contain $\mathcal{C}_\mathcal{E}(B) - 1$ operators that do not commute with all operators $c_i \in \mathcal{E}$ (note that the operators from $\mathcal{E}$ anticommute). This completes the proof.

□

*Proof of Theorem A.1.* We define

$$\mathcal{E} := \{a_I \mid I \in \text{occ}\} \cup \{a_A^\dagger \mid A \in \text{virt}\}. \tag{A.10}$$

All elements from $\mathcal{E}$ anticommute by (A.4), and all excitation operators $X_\alpha$ are strings built from elements of $\mathcal{E}$. Using the expression (A.5), we obtain

$$\begin{aligned}e^{-T} H e^T = \sum_{n=0}^{\infty} \frac{1}{n!} [H,T]_{(n)} &= \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{P,Q \in \mathcal{I}} h_{PQ} \, [a_P^\dagger a_Q, \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha]_{(n)} \\ &\quad + \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{P,Q,R,S \in \mathcal{I}} \langle PQ||RS\rangle [a_P^\dagger a_Q^\dagger a_R a_S, \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha]_{(n)}.\end{aligned}$$

For each string $a_P^\dagger a_Q$, there holds $\mathcal{C}_\mathcal{E}(a_P^\dagger a_Q) \leq 2$. We observe that the commutator is linear in its first argument, so iterating Lemma A.3 gives

$$\mathcal{C}_\mathcal{E}\Big(\big[[a_P^\dagger a_Q, X_{\alpha_1}], X_{\alpha_2}\big]\Big) = 0, \qquad \Big[\big[[a_P^\dagger a_Q, X_{\alpha_1}], X_{\alpha_2}\big], X_{\alpha_3}\Big] = 0$$

for all $\alpha_1, \alpha_2, \alpha_3 \in \mathcal{M}_k^*$, so

$$[a_P^\dagger a_Q, \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha]_{(n)} = 0$$

follows for $n \geq 3$. To the iterated commutators $[a_P^\dagger a_Q^\dagger a_R a_S, \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha]_{(n)}$, an analogous argument applies to show that those of order $n \geq 5$ must give zero contributions, so the proof is finished.

□

**Remark A.4.** We remark that the representation (A.2) coincides with the Taylor expansion of the $C^\infty$-function $g(T) = e^{-T} A e^T$ at $T = 0$: more generally, it is given for arbitrary $S \in B(\mathbb{H}^1)$ by $g(S+T) = e^{-T-S} A e^{T+S} = \sum_{i=0}^4 1/n! [e^{-S} A e^S, T]_{(n)}$. In particular, this implies $f^{(5)} \equiv 0$ for the CC function.

**(iv) Evaluation of the iterated commutators.** To apply solvers like e.g. the below simple inexact Newton's method to solve the root problem (2.20), the Coupled Cluster function and thus, by Theorem A.1, the expression

$$f(t) \;=\; \sum_{n=0}^{4} \frac{1}{n!} \langle \Psi_\mu, [H,T]_{(n)} \Psi_0 \rangle \;=\; \sum_{n=0}^{4} \frac{1}{n!} \langle \Psi_0, X_\mu^\dagger [H,T]_{(n)} \Psi_0 \rangle \tag{A.11}$$

has to be evaluated for all $\mu \in \mathcal{M}^*$. This is a nontrivial task, and for sake of brevity, we only sketch the canonical proceeding here and refer the reader to the comprehensive introduction [22] and the references given therein for deeper insight. To evaluate (A.11), *Wick's theorem*, proven e.g. in [40] and based on the anticommutator relations (A.4), is the fundamental tool used to successively reorder the operator strings contained in $X_\mu^\dagger [H,T]_{(n)}$ to sums of *normal-ordered* strings (i.e. strings where for $\mathcal{E}$ defined by (A.10), all operators $b \in \mathcal{E}$ are to the left of all operators $b \notin \mathcal{E}$). Normal-ordered strings give a zero contribution to (A.11), and the remainder term is a sum of so called "fully contracted terms", containing no annihilation/creation operators anymore as a result of various anticommutators arising in the ordering process. The task is now to determine all of those admissible fully contracted terms that yield a nonzero distribution to (A.11), and this boils down to choosing the right indices of matrix elements of $\hat{H}$ and of up to four different cluster amplitudes $t_\nu$ that contribute to each $\mu$-th component of $f(t)$ according to certain rules. This combinatorial task is nontrivial, and especially tedious to implement because the fully contracted terms feature various combinations of signs arising from the anticommutation laws. Therefore, an approach popularized in [47] is normally used to rewrite the equations as diagrams (see also [22]); then, computable expressions are derived from these diagrams by a fixed set of rules, either by hand or automatedly as e.g. in [4,46]. To give the reader an impression of the resulting equations, we depicted the update equations for the energy and the $T_1$-/$T_2$-amplitudes for the frequently used CCSD procedure in

Figure A. In this, the coefficients $f_{PQ}$ are those determined by the according one-particle operator $F$. Evaluation for the "doubles" amplitudes $f(t)_{IJ}^{AB}$ is an $N^6$ step if one supposes that the number of virtual orbitals in the chosen discretisation is proportional to $N$. Note the most expensive summation step (but not the only $N^6$ step) is given by the term $\frac{1}{2}\sum_{CD}\langle AB\|CD\rangle t_{IJ}^{CD}$ contributing to $f(t)_{IJ}^{AB}$ (see the second line). This step consists of a summation over $V^2$ terms for each of the $N^2V^2$ amplitudes, so that the evaluation of this contribution is a step of complexity $N^2V^4$, which usually consumes (due to the constants entering by $V = C \cdot N$) about $70 - 90\%$ of the overall computation time. Efficient factorization of the CC equations is another topic of its own, cf. e.g. the references in [22].

**(iv) Newton's method for the CC function.** To solve the CC root equation (2.20), it is common practice to use an inexact Newton's method with the (lifted, shifted) Fock matrix as approximate Jacobian or related Jacobi-like schemes. With the results of the previous sections, we now obtain a convergence result for the more general setting, by which we close this present section.

**Corollary A.5.** *(Convergence of a quasi-Newton method)*

*Let $P : \mathbb{V} \to \mathbb{V}'$ be any linear bounded coercive linear mapping. If $E^*$ is a simple eigenvalue and $\Psi_0$ is close enough to $\underline{\Psi}$, there is an $\alpha > 0$ such that the damped inexact Newton's method*

$$x_{n+1} \;=\; x_n - \alpha P^{-1} f(x_n) \tag{A.12}$$

*with starting value $\Psi_0$ converges to $\underline{\Psi}$. If $\|Df(t^*) - P\|$ is small enough, $\alpha = 1$ is a possible choice.*

The proof is identical with that for the finite dimensional case, which can be derived e.g. from Theorem 8.2.2 in [23], so it is omitted. We only note that also in the convergence estimates for Newton's method, the decisice constants are the local Lipschitz constant $L$ and the monotonicity constant $\gamma$ of the CC function.

□

$$
\begin{aligned}
E(t) &= \langle \Psi_0, H\Psi_0\rangle + \sum_{IA} f_{IA} t_I^A + \frac{1}{4}\sum_{IJAB}\langle IJ\|AB\rangle t_{IJ}^{AB} + \frac{1}{2}\sum_{IJAB}\langle IJ\|AB\rangle t_I^A t_J^B,\\
f(t)_I^A &= f_{IA} + \sum_C f_{AC} t_I^C - \sum_K f_{KI} t_K^A + \sum_{KC}\langle KA\|CI\rangle t_C^K + \sum_{KC} f_{KC} t_{IK}^{AC}\\
&+ \frac{1}{2}\sum_{KCD}\langle KA\|CD\rangle t_{KI}^{CD} - \frac{1}{2}\sum_{KLC}\langle KL\|CI\rangle t_{KL}^{CA} - \sum_{KC} f_{KC} t_I^C t_K^A - \sum_{KLC}\langle KL\|CI\rangle t_K^C t_L^A\\
&+ \sum_{KCD}\langle KA\|CD\rangle t_K^C t_I^D - \sum_{KLCD}\langle KL\|CD\rangle t_K^C t_I^D t_L^A + \sum_{KLCD}\langle KL\|CD\rangle t_C^K t_{LI}^{DA}\\
&- \frac{1}{2}\sum_{KLCD}\langle KL\|CD\rangle t_{KI}^{CD} t_L^A - \frac{1}{2}\sum_{KLCD}\langle KL\|CD\rangle t_{KL}^{CA} t_I^D\\
f(t)_{IJ}^{AB} &= \langle IJ\|AB\rangle + \sum_C \left(f_{BC} t_{IJ}^{AC} - f_{AC} t_{IJ}^{BC}\right) - \sum_K \left(f_{KJ} t_{IK}^{AB} - f_{KI} t_{JK}^{AB}\right)\\
&+ \frac{1}{2}\sum_{KL}\langle KL\|IJ\rangle t_{KL}^{AB} + \frac{1}{2}\sum_{CD}\langle AB\|CD\rangle t_{IJ}^{CD} + P(IJ)P(AB)\sum_{KC}\langle KB\|CJ\rangle t_{IK}^{AC}\\
&+ P(IJ)\sum_C\langle AB\|CJ\rangle t_I^C - P(AB)\sum_K\langle KB\|IJ\rangle t_A^K\\
&+ \frac{1}{2}P(IJ)P(AB)\sum_{KLCD}\langle KL\|CD\rangle t_{IK}^{AC} t_{LJ}^{DB} + \frac{1}{4}\sum_{KLCD}\langle KL\|CD\rangle t_{IJ}^{CD} t_{KL}^{AB}\\
&+ \frac{1}{2}P(AB)\sum_{KLCD}\langle KL\|CD\rangle t_{IJ}^{AC} t_{KL}^{BD} - \frac{1}{2}P(IJ)\sum_{KLCD}\langle KL\|CD\rangle t_{IK}^{AB} t_{JL}^{CD}\\
&+ \frac{1}{2}P(AB)\sum_{KL}\langle KL\|IJ\rangle t_K^A t_L^B + \frac{1}{2}P(IJ)\sum_{CD}\langle AB\|CD\rangle t_I^C t_J^D\\
&- P(IJ)P(AB)\sum_{KC}\langle KB\|IC\rangle t_K^A t_J^C + P(AB)\sum_{KC} f_{KC} t_K^A t_{IJ}^{BC}\\
&+ P(IJ)\sum_{KC} f_{KC} t_I^C t_{JK}^{AB} - P(IJ)\sum_{KLC}\langle KL\|CI\rangle t_K^C t_{LJ}^{AB}\\
&+ P(AB)\sum_{KCD}\langle KA\|CD\rangle t_K^C t_{IJ}^{DB} + P(IJ)P(AB)\sum_{KCD}\langle AK\|DC\rangle t_I^D t_{JK}^{BC}\\
&+ P(IJ)P(AB)\sum_{KLC}\langle KL\|IC\rangle t_L^A t_{JK}^{BC} + \frac{1}{2}P(IJ)\sum_{KLC}\langle KL\|CJ\rangle t_I^C t_{KL}^{AB}\\
&- \frac{1}{2}P(AB)\sum_{KCD}\langle KB\|CD\rangle t_K^A t_{IJ}^{CD} + \frac{1}{2}P(IJ)P(AB)\sum_{KLC}\langle KB\|CD\rangle t_I^C t_K^A t_J^D\\
&+ \frac{1}{2}P(IJ)P(AB)\sum_{KLC}\langle KL\|CJ\rangle t_I^C t_K^A t_L^B - P(IJ)\sum_{KLCD}\langle KL\|CD\rangle t_K^C t_I^D t_{LJ}^{AB}\\
&- P(AB)\sum_{KLCD}\langle KL\|CD\rangle t_K^C t_L^A t_{IJ}^{DB} - \frac{1}{4}P(IJ)\sum_{KLCD}\langle KL\|CD\rangle t_I^C t_J^D t_{KL}^{AB}\\
&+ \frac{1}{4}P(AB)\sum_{KLCD}\langle KL\|CD\rangle t_K^A t_L^B t_{IJ}^{CD} + P(IJ)P(AB)\sum_{KLCD}\langle KL\|CD\rangle t_I^C t_L^B t_{KJ}^{AD}\\
&+ \frac{1}{4}P(IJ)P(AB)\sum_{KLCD}\langle KL\|CD\rangle t_I^C t_K^A t_J^D t_L^B
\end{aligned}
$$

FIGURE 1. The CCSD equations for the CC energy $E(t)$ and for the $T_1, T_2$ amplitudes $f(t)_I^A, f(t)_{I,J}^{A,B}$, $(I,J \in \text{occ}, A,B \in \text{virt})$. In this, $P(IJ)f(I,J) := f(I,J) - f(J,I)$.

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