



Adaptive Coupled Cluster Method and CI Method for the Solution of the Electronic Schroedinger Equation

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The electronic Schrödinger equation plays a fundamental role in molecular physics. It describes the stationary non-relativistic quantum mechanical behavior of an N electron system in the electric field generated by the nuclei. The *Coupled Cluster Method* has been developed for the numerical computation of the ground state energy and wave function. It provides a powerful tool for high accuracy electronic structure calculations. The present paper aims to provide a convergence analysis of this method. Under additional assumptions quasi-optimal convergence of the projected coupled cluster solution to the full CI solution and also to the exact wave function can be shown in the Sobolev H^1 norm. The error of the ground state energy computation is obtained by an Aubin Nitsche type approach.

Recent developments in science and technology, in particular in chemistry, molecular biology, material sciences or semi-conductor devices, are requesting reliable computations of molecular behavior. On an atomic or molecular length scale, the physics is governed by the laws of quantum mechanics. Consequently, numerical modeling of such processes should be based on *first principles* of quantum mechanics. The basic equation for a quantitative description of atomistic and molecular phenomena of interest is the *electronic Schrödinger equation*. It describes the stationary and non-relativistic behavior of an ensemble of N electrons in an electric field resulting from fixed nucleons,

$$\mathcal{H}\Psi = \sum_{i=1}^N \left[-\frac{1}{2}\Delta_i - \sum_{j=1}^M \frac{Z_j}{|\mathbf{x}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{j \neq i}^N \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right] \Psi = E\Psi .$$

The ground state energy of a given N -electron system, which is the eigenvalue of the lowest eigenstate of the Schrödinger-Hamilton operator is of major interest,

$$E_0 = \min_{\langle \Psi, \Psi \rangle = 1} \langle \mathcal{H}\Psi, \Psi \rangle .$$

Since the corresponding wave function depends on $3N$ spatial variables and N two-valued spin variables

$$\Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N) \quad , \quad \Psi : \mathbb{R}^{3N} \otimes S^N \rightarrow \mathbb{C} \text{ resp. } \mathbb{R} \quad , \quad \langle \Psi, \Psi \rangle = 1 \quad ,$$

not to mention its lack of smoothness, its numerical approximation is a rather difficult and challenging task. Usually it is approximated by sums anti-symmetric tensor products $\Psi = \sum_{k=1}^{\infty} c_k \Psi_k$ with Slater determinants Ψ_k defined by

$$\Psi_k(\mathbf{x}_1, s_1, \dots, \mathbf{x}_N, s_N) = \varphi_{1,k} \wedge \dots \wedge \varphi_{N,k} = \frac{1}{\sqrt{N!}} \det(\varphi_{i,k}(\mathbf{x}_j, s_j))_{i,j=1}^N \quad ,$$

$\langle \varphi_{i,k}, \varphi_{j,k} \rangle = \delta_{i,j}$, with N orthonormal functions φ_i , $i = 1, \dots, N$ called *spin orbitals* $\varphi_i : \mathbb{R}^3 \times \{\pm \frac{1}{2}\} \rightarrow \mathbb{C}(\mathbb{R})$, $i = 1, \dots, N$. In contrast to the CI (Configuration Interaction) method, which consists in a linear parametrization and a corresponding Galerkin method, the *Coupled Cluster* (CC)-method is based on an exponential parametrization of the wave function,

$$\Psi = e^T \Psi_0 \quad , \quad T = \sum_{i=1}^N T_i = \sum_{\mu \in \mathcal{J}} t_{\mu} X_{\mu}$$

for given reference determinant Ψ_0 and excitation operators X_{μ} and unknown amplitudes t_{μ} satisfying the *amplitude equations*

$$0 = \langle \Psi_{\mu}, e^{-T} H \Psi \rangle = \langle \Psi_{\mu}, e^{-T} H e^T \Psi_0 \rangle =: \mathbf{f}_{\mu}(\mathbf{t}) \quad , \quad \mathbf{t} = (t_{\nu})_{\nu \in \mathcal{J}} \quad , \quad \mu, \nu \in \mathcal{J} .$$

Restricting the ansatz and the above amplitude equations to a relevant subset of excitation $\mathcal{J}_h \subset \mathcal{J}$, usually consisting of single and double excitations, yields to the *projected CC method*, e.g CCSD. In contrast to truncated CI methods, like CISD, the projected is *size consistent*, due to exponential parametrization. Nowadays the projected CC approach constitutes the method of choice for high resolution wave function computation in electronic structure calculation, at least in cases where dynamical correlation is dominating. However, it performs poorly

in some cases, where a single reference Slater determinant is not sufficient. Due to the authors knowledge, the authors paper [4] was the first attempt to analyse the (*Projected Coupled*) *Cluster method* rigorously from a numerical analysis point of view. For the analysis of the CC method, as well as in practice, presented in [4], the (approximate) Hartree Fock wave function is considered as a reference Slater determinant. Based on the established convergence of the full CI solution towards the exact wave function by the full CI solution, in a second step, the convergence of the projected CC solution to the full CI solution is considered in detail. In particular, a weighted l_2 -norm for the *coupled cluster amplitudes* $\|\mathbf{t}\|_V$ has been introduced, which are shown to be equivalent to the H^1 Sobolev norm of the approximate wave functions in a certain extent. With this notion at hand, the projected CC method can be interpreted as a Galerkin method for a non-linear function $\mathbf{f} : V \rightarrow V'$ seeking $\mathbf{t}_h \in V_h$ s.t.

$$\langle \mathbf{f}(\mathbf{t}_h), \mathbf{v}_h \rangle = 0 \quad \forall \mathbf{v}_h \in V_h \subset V.$$

Under an additional assumption of strict monotonicity of the amplitude function, quasi-optimal convergence of the projected CC method is concluded.

Theorem ([4]) (a priori estimate) If $\mathbf{f}(\mathbf{t}) = \mathbf{0}$ and \mathbf{f} is (locally) strictly monotone at \mathbf{t} and the solution of the Galerkin scheme \mathbf{t}_h satisfies $\|\mathbf{t} - \mathbf{t}_h\|_V \leq \delta$ then it satisfies

$$\|\mathbf{t} - \mathbf{t}_h\|_V \lesssim \inf_{\mathbf{v} \in \mathbb{R}^{dJ}} \|\mathbf{t} - \mathbf{v}_h\|_V.$$

and

$$\|\Psi - \Psi_h\|_{H^1} \lesssim \inf_{\mathbf{v} \in \mathbb{R}^L} \|\Psi - e^{\sum_{\mu \in \mathcal{J}_h} v_\mu X_\mu} \Psi_0\|_{H^1}.$$

Since convergence problems are reported for the CC method in presence of statistical correlation, convergence might depend on the actual molecular configuration. Therefore setting such an assumption seems to be reasonable. Whether this might be necessary or not is not clear yet.

Since the ground state energy is a functional of the amplitudes

$$J(\mathbf{t}) := E(\mathbf{t}) := \langle \Psi_0, H(1 + T_2 + \frac{1}{2}T_1^2)\Psi_0 \rangle,$$

in order to estimate the convergence of the computed eigenvalue to the exact ground state energy, the *dual weighted residual* approach, introduced by Rannacher et al., has been applied for the derivation of sharp a priori estimates. Defining the *Lagrange functional*

$$L(\mathbf{t}, \mathbf{a}) := J(\mathbf{t}) - \langle \mathbf{f}(\mathbf{t}), \mathbf{a} \rangle, \quad \mathbf{t} \in V', \quad \mathbf{a} \in V,$$

its stationary points are given by the solution of the *amplitude equation* $\mathbf{f}(\mathbf{t}) = \mathbf{0}$ and the *dual equation* for $\mathbf{a} \in V$

$$\mathbf{f}'[\mathbf{t}]^\top \mathbf{a} = -(J'[\mathbf{t}]) \in V'.$$

The error of the energy functional obtained by the Galerkin solutions $\mathbf{t}_h, \mathbf{a}_h$ can be expressed by the corresponding residuals

$$|J(\mathbf{t}) - J(\mathbf{t}_h)| = \frac{1}{2} \langle \mathbf{r}(\mathbf{t}_h), \mathbf{a} - \mathbf{b}_h \rangle + \frac{1}{2} \langle \mathbf{r}^*(\mathbf{t}_h, \mathbf{a}_h), (\mathbf{t} - \mathbf{u}_h) \rangle + \mathcal{R}^3, \quad \forall \mathbf{u}_h, \mathbf{b}_h \in V_h,$$

with a cubic remainder term \mathcal{R}^3 , which implies the following result.

Theorem ([4]) The error in the energy $E = J(\mathbf{t})$ and the discrete energy $E_h = J(\mathbf{t}_h)$ can be estimated by

$$\begin{aligned} |E - E_h| &\lesssim \|\mathbf{t} - \mathbf{t}_h\|_V \|\mathbf{a} - \mathbf{a}_h\|_V + (\|\mathbf{t} - \mathbf{t}_h\|_V)^2 \\ &\lesssim \inf_{\mathbf{u}_h \in V_h} \|\mathbf{t} - \mathbf{u}_h\|_V \inf_{\mathbf{b}_h \in V} \|\mathbf{a} - \mathbf{b}_h\|_V + \\ &\quad + \left(\inf_{\mathbf{u}_h \in V_h} \|\mathbf{t} - \mathbf{u}_h\|_V \right)^2. \end{aligned}$$

Originally, the *dual weighted residual method* has been developed for the design of local a posteriori error estimators for adaptive finite element methods, which are used to optimize the finite element meshes for computation of certain functionals of the solution. However adaptive finite element method (FEM) techniques cannot be transferred immediately to the solution of the electronic Schrödinger equation. Perhaps, instead of truncating with respect to the excitation level one needs nonlinear approximation procedures for optimizing the basis sets, and even more significant, for an automatic selection of those amplitudes which contributes most to the ground energy. An alternative is provided by nonlinear best n-term approximation strategies introduced by Cohen, Dahmen, DeVore.

The amplitude equations

$$0 = \mathbf{f}_\mu(\mathbf{t}) = \langle \Psi_\mu, e^{-T} H e^T \Psi_0 \rangle = \langle \Psi_\mu, [\mathcal{F}, T] \Psi_0 \rangle + \langle \Psi_\mu, e^{-T} U e^T \Psi_0 \rangle$$

are of the form $\mathbf{f}(\mathbf{t}) = \mathbf{F}\mathbf{t} - \Phi(\mathbf{t}) = \mathbf{0}$ which can be solved iteratively by an augmented Newton type scheme $\mathbf{t}^{n+1} := \mathbf{F}^{-1}\Phi(\mathbf{t}^n)$, which in turn has to be performed only approximatively according to best n-term strategies.

The same strategy applies also to the CI method still in an almost size extensive way. In two recent papers on adaptive best n-term algorithm for the computation of the lowest eigenvalue and eigenstate has been developed [1, 2]. Regularity providing best n-term convergence rates has been obtained by Yserentant and also in [3].

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