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Adaptive methods in quantum chemistry

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Abstract

In this article, we summarize the results of our numerical analysis for various adaptive schemes in electronic structure calculations. Starting from a general form of iterative schemes used in quantum chemistry, we discuss miscellaneous features which are of importance when passing to an adaptive version of an algorithm in order to provide rigorous estimates. The key features are maintainance of convergence under small perturbations while keeping control of the computational complexity.

As a prototype for correlation methods, we consider the configuration interaction (CI) method and discuss a quasi-optimal algorithm for computation of the ground state energy. Our analysis of the coupled cluster method shows that various properties of the CI method can be transferred hereunto as well. First numerical examples demonstrate the potential of the coupled cluster residual, measured in a norm on the dual space, as an error estimator. These studies are supplemented by our result for the best N-term approximation of electron-pair correlations by wavelets.

For Hartree-Fock and Kohn-Sham methods, we discuss our results of the convergence analysis for a direct minimization scheme, the best N-term approximation of orbitals and s^*-compressibility of the Fock operator which altogether may serve as a basis for an adaptive version of these methods.

Zusammenfassung

In diesem Artikel fassen wir die Ergebnisse unserer numerischen Analysis für verschiedene adaptive Algorithmen zur Elektronenstrukturberechnung zusammen. Ausgehend von einer allgemeinen Form von Iterationsverfahren diskutieren wir diverse Aspekte, die beim Übergang zu einer adaptiven Version eines Algorithmus beachtet werden müssen, um strenge Abschätzungen geben zu können. Die wichtigsten Punkte sind hierbei, die Konvergenz des Algorithmus unter kleinen Störungen zu erhalten, während die Komplexität des Algorithmus unter Kontrolle gehalten wird.

Als Prototyp für Korrelationsmethoden beschäftigen wir uns mit der *Configuration Interaction* (CI) Methode und erläutern einen quasi-optimalen Algorithmus zur Berechnung der Grundzustandsenergie. Unsere Analyse der *Coupled Cluster*-Methode zeigt, dass sich diverse Eigenschaften der CI-Methode auch hierauf übertragen lassen. Erste numerische Beispiele demonstrieren das Potential des Coupled-Cluster-Residuums, gemessen in einer Norm auf dem Dualraum, als Fehlerschätzer. Diese Studien werden ergänzt durch unser Resultat über die beste N-Term-Approximation der Elektronenpaarkorrelation durch Wavelets.

Für Hartree-Fock- und Kohn-Sham-Methoden diskutieren wir die Ergebnisse unserer Konvergenzanalyse für ein direktes Minimierungsschema, die beste N-Term-Approximation für Orbitale und die s^*-Komprimierbarkeit des Fock-Operators. Diese Ergebnisse können als Grundlage für eine adaptive Version dieser Methoden dienen.

1 Introduction

Concepts of adaptivity have found widespread use in quantum chemistry, ranging from the construction of *Gaussian-type orbital* (GTO) basis sets, see e.g. the development of correlation consistent bases [1, 2, 3], to linear scaling methods in *density functional theory* (DFT) [4, 5, 6, 7, 8, 9], selective *configuration interaction* (CI) methods [10, 11, 12, 13, 14, 15, 16, 17, 18] and local correlation methods based on many-body perturbation or *coupled cluster* (CC) theory [19, 20, 21, 22]. In most of these methods, the adaptive procedure is based on physical insights and empirical evidence from numerical simulations; a rigorous mathematical justification, however, is usually missing. Often, familiar concepts lose a lot of their original power if one tries to put them in a rigorous mathematical framework. As a typical example, let us mention GTO bases, for which highly sophisticated optimization schemes have been devised in quantum chemistry. However, even systematic GTO basis sets like the correlation consistent bases mentioned before do not meet the requirements of a Riesz basis frequently used in numerical analysis. Riesz bases are not only complete, but remain stable even in the limit of an infinitely dimensional space. Putting GTO bases in a rigorous setting, which can be done e.g. within *approximate approximation theory* [23], deprives them to a certain extent of their flexibility and adaptivity. Unfortunately, similar drawbacks can be brought forward to most of the adaptive methods mentioned before. Therefore, we will not shoulder the monumental and perhaps questionable task to provide a rigorous mathematical analysis for the adaptive approaches used in nowadays quantum chemistry. Instead it seems more favourable to us to perform the mathematical analysis of methods used in electronic structure calculations within settings familiar to numerical analysis. Of course, this might lead to adaptive methods which are not fully competitive from a practical point of view; for example, working with a systematic Riesz basis instead of GTO bases requires from the onset larger basis sets and the benefit of systematic improvement might be a distant prospect. However, we have the more realistic prospect that our rigorous analysis provides new and hopefully enlightening perspectives on standard adaptive methods, which we reckon cannot be obtained in another way.

The paper is organized as follows: In Section 2, we present a general outline of iterative adaptive algorithms and discuss some of the basic mathematical concepts involved in their numerical analysis. Turning to concrete examples in Section 3, we discuss adaptive CI and CC algorithms. Section 4 deals with the numerical analysis of *Hartree-Fock* (HF) and *Kohn-Sham* (KS) equations which paves the way for adaptive algorithms with optimal computational complexity. For the convenience of the reader we have summarized essential background material from functional analysis in Appendix A.

2 Design of adaptive algorithms

The following discussion of adaptive algorithms is based on the general assumption that the underlying problem can be treated in terms of an iterative solution scheme of the abstract form:

Iterative Algorithm (I)

Require: *Initial iterate* $\mathbf{x}^{(0)} \in V$*;*
for $n = 0, 1, \ldots$ *until convergence do*
(1) *From* $\mathbf{x}^{(n)}$ *and given data, compute update* $\Delta\mathbf{x}^{(n)}$*.*
(2) *Update* $\mathbf{x}^{(n+1)} = \mathbf{x}^{(n)} + \Delta\mathbf{x}^{(n)}$*.*
endfor

In most cases of interest, step (1) consists in matrix-vector multiplications or function evaluations to compute a residual-like quantity; for example, in the case of CI methods, this role is played by $\mathbf{r}^{(n)} = \mathbf{H}\mathbf{x}^{(n)} - E^{(n)}\mathbf{x}^{(n)}$, in CC methods it is the evaluation of the CC function $\mathbf{r}^{(n)} = \mathbf{g}(\mathbf{x}^{(n)})$, cf. Section 3.2 below. To compute the update, this residual is usually multiplied by a preconditioning matrix. In electronic structure calculations this role is often played by the inverse of the shifted Fock matrix, i.e. $\Delta\mathbf{x}^{(n)} = \mathbf{F}^{-1}\mathbf{r}^{(n)}$ Note that after step (2), some algorithms, e.g. those for HF or KS equations, require a supplementary step like normalization or orthogonalization of the iterates in order to fulfil additional constraint conditions.

The objective of an adaptive algorithm is the usage of sparse quantities in every step of algorithm (I) and thereby a rigorous control of the computational complexity. In a pseudo-algorithmic form, an adaptive algorithm may be formulated in the following way:

Adaptive Algorithm (II)

Require: *Sparse initial iterate* $\mathbf{x}^{(0)} \in V$*;*
for $n = 0, 1, \ldots$ *until convergence do*
(1) *APPLY-step: From* $\mathbf{x}^{(n)}$ *and compressed data, compute with optimal computational complexity an approximate update* $\Delta_\epsilon\mathbf{x}^{(n)}$*.*
(2) *Update* $\mathbf{x}^{(n+1)} = \mathbf{x}^{(n)} + \Delta_\epsilon\mathbf{x}^{(n)}$*.*
(3) *COARSE-step: If supp*$(\mathbf{x}^{(n+1)})$ *gets too big, sparsify* $\mathbf{x}^{(n+1)}$ *by thresholding.*
endfor

Such an adaptive algorithm features two approximation steps, i.e., the computation of an approximate residual instead of the exact one, and an intermediate coarsening step to keep sparsity of the iterates. The general goal is (i) to construct an adaptive algorithm in the fashion of (II), which converges to the limit of the exact algorithm (I) up to a controllable error tolerance ε while (ii) it is based on the usage of sparse quantities to control the computational complexity of the algorithm. Let us investigate these two points in more detail:

(i) Maintaining convergence: Let us assume for illustration that for the basic iteration scheme (I), we have linear convergence, i.e., the

error reduces by a fixed factor $c < 1$ in each step,

$$\mathrm{err}\big(\mathbf{x}^{(n+1)}\big) = \mathrm{err}\big(\mathbf{x}^{(n)} + \Delta\mathbf{x}^{(n)}\big) \ \leq c\ \mathrm{err}\big(\mathbf{x}^{(n)}\big). \tag{2.1}$$

For a subadditive error measure, we may estimate the error of an approximate iterate $\mathbf{x}_\epsilon^{(n+1)} = \mathbf{x}^{(n)} + \Delta_\epsilon\mathbf{x}^{(n)}$ by

$$\mathrm{err}\big(\mathbf{x}_\epsilon^{(n+1)}\big) \quad \leq \quad \mathrm{err}\big(\mathbf{x}^{(n)} + \Delta\mathbf{x}^{(n)}\big) + \mathrm{err}\big(\Delta_\epsilon\mathbf{x}^{(n)} - \Delta\mathbf{x}^{(n)}\big), \tag{2.2}$$

so that convergence can be maintained (with a different constant $\tilde{c}$ still smaller than 1) if we are for instance able to control the approximation error by

$$\mathrm{err}\big(\Delta_\epsilon\mathbf{x}^{(n)} - \Delta\mathbf{x}^{(n)}\big) \ < \ \epsilon\ \mathrm{err}\big(\mathbf{x}^{(n)}\big) \ \text{ with } \tilde{c} = c + \epsilon < 1.$$

In many cases, it can be shown that the current error may be estimated from above and below by the residual (measured in an appropriate norm), so that the residual may be utilized to estimate the accuracy of the adaptive approximation needed in order to maintain convergence.
From a mathematical point of view, this procedure raises the following questions: To lay a basis for error estimates like (2.2), it has first of all to be shown that convergence results like (2.1) hold at least in a neighbourhood of the solution. Of course, this is also a question of its own interest. This significance of convergence analysis is contrasted by the scarcity of rigorous convergence analysis for methods utilized in quantum chemistry. Next, the relation between residuals and the actual errors mentioned before has to be established. Finally, we have to investigate the mutual interplay between errors in the iterates and the error in the quantity of interest, i.e., in our case the eigenvalues of the operators under consideration.

(ii) Control of complexity: Once convergence has been established for the full, still infinite dimensional problem, the principal idea is to restrict each iteration step in an approximate manner to a finite dimensional subspace in order to control the computational complexity of the whole scheme. This requires that all components of the iteration scheme allow for sparse approximations which are preserved during the operations of the iteration step.

(a) Sparse representability of iterates: In order to keep the number of nonzero coefficients $x_i^{(n)} \neq 0$ of an iterate $\mathbf{x}^{(n)}$ as small as possible, we need an adaptive approximation theory for the final solution and the intermediate iterates. For a certain class of stable Riesz bases, e.g. wavelets, this can be accomplished in the framework of *best-N-term approximation* theory. In this paragraph we give a short outline of this theory and discuss its application for adaptive algorithms. For a detailed exposition of this subject we refer to [24].

Given a function f which can be exactly represented in a Riesz basis

$$B := \{\zeta_i : i \in \mathcal{I}\}, \tag{2.3}$$

we denote by $\mathbf{f}$ the coefficient vector with respect to B. The smallest error

$$\sigma_N(\mathbf{f}) := \inf_{\mathbf{f}_N \in \Sigma_N} \|\mathbf{f} - \mathbf{f}_N\|_{\ell_2} \tag{2.4}$$

that can be achieved for the approximation of $\mathbf{f}$ by a linear combination of at most N basis functions, i.e. by functions taken from the nonlinear subset

$$\Sigma_N := \left\{ \sum_{j \in \mathcal{J}} c_j \zeta_j \mid \mathcal{J} \subset \mathcal{I}, |\mathcal{J}| \leq N \right\}, \tag{2.5}$$

is the error of the best N-term approximation of $\mathbf{f}$ in $\ell_2(\mathcal{I})$.

The approximation error $\sigma_N(\mathbf{f})$ for the coefficient vector is given with respect to the Euclidean norm on $\ell_2(\mathcal{I})$. For a Riesz basis B this error is equivalent to the approximation error of the function f in the Hilbert space L_2 or the Sobolev space H^1 (see Appendix A) depending on the weights assigned to the basis functions. In order to characterize all functions for which the error of their best N-term approximation decays at least as N^{-s} for some $s > 0$ we introduce the (quasi-)seminorm

$$|\mathbf{f}|_{\mathcal{A}^s} := \sup_{N \in \mathbb{N}} N^s \sigma_N(\mathbf{f}) \tag{2.6}$$

This seminorm can be used to define the best N-term approximation spaces

$$\mathcal{A}^s := \{\mathbf{f} \in \ell_2(\mathcal{I}) : ||\mathbf{f}||_{\mathcal{A}^s} := ||\mathbf{f}|| + |\mathbf{f}|_{\mathcal{A}^s} < \infty\},$$

which are (quasi-)Banach spaces for all $s > 0$. Another way to view at this is the following: In order to approximate a given function f with coefficient vector $\mathbf{f} \in \mathcal{A}^s$ with an accuracy ε it requires at most $N_\varepsilon = \varepsilon^{-1/s} |\mathbf{f}|_{\mathcal{A}^s}^{1/s}$ nonzero entries. This fundamental relation

$$\text{accuracy } \varepsilon \quad \longleftrightarrow \quad (|\mathbf{f}|_{\mathcal{A}^s}/\varepsilon)^{1/s} \text{degrees of freedom} \tag{2.7}$$

reflects the desired sparsity of the iterates in $\ell_2(\mathcal{I})$ and serves as a guideline for the construction of adaptive algorithms.

Due to the norm equivalence of the function spaces L_2 or H^1 with the discrete $\ell_2(\mathcal{I})$ norm of the coefficient vector for an appropriate Riesz basis B, a best N-term approximation of the coefficient vector, which can be achieved by simply selecting the N largest coefficients, gives a quasi-best approximation of the corresponding function in Σ_N. In order to predict quasi-optimal convergence rates of adaptive algorithms it is therefore necessary to specify the best N-term approximation spaces $\mathcal{A}^s$ to which the final solution and all intermediate iterates belong. The seminorm (2.6) is often not convenient for this purpose. As an alternative it is possible to choose a subspace $\mathcal{A}_q^s \subset \mathcal{A}^s$ with $\frac{1}{q} = s + \frac{1}{2}$ which is only slightly smaller, i.e. $\mathcal{A}^{s'} \subset \mathcal{A}_q^s \subset \mathcal{A}^s$ for all $0 < s' < s$, but easier to handle. The subspaces

$\mathcal{A}_q^s$ can be identified with certain Besov spaces [24] which provide an alternative to Sobolev spaces to characterize the smoothness of a function. In contrast to Sobolev spaces of higher order of regularity, the less stringent Besov spaces of comparable order allow e.g. for a finite number of discontinuities in the function or its derivatives provided that the function is sufficiently regular in between. This is of special significance for the point-like singularities at the electron-nuclear cusps.

Among the most popular realizations of Riesz bases are wavelets. The corresponding multiresolution analysis provides a convenient setting for the development of adaptive algorithms. We refer to the monographs [25, 26] for a detailed exposition of this subject.

(b) Complexity of matrix-vector operations: Computation of the residual from an iterate $\mathbf{x}^{(n)}$ involves (possibly a series of) matrix-vector operations with an $M \times M$ matrix. For the sparse case, these operations may be executed at a favourable expense of $m \cdot \mathrm{supp}(\mathbf{x}^{(n)})$ with $m << M$, while for the non-sparse case, $M \cdot \mathrm{supp}(\mathbf{x}^{(n)})$ products have to be computed. If the matrix is *quasi-sparse* or s^**-compressible*, i.e., the coefficients decay in a certain manner, a more elaborate scheme selecting the important contributions to the product may be utilized to approximate matrix-vector multiplications at an expense no higher than $\mathcal{O}(\mathrm{supp}(\mathbf{x}^{(n)}))$[27]. To rely on these schemes, an analysis of the properties of the involved operators, i.e. the Hamiltonian H resp. Fock operator, in the mathematical context of s^**-compressibility* is in order. To explain this terminology, we assume a fixed basis set (2.3), which provides us with a Hamiltonian matrix $\mathbf{H}$ in the Galerkin discretization (which is infinite dimensional if we use a complete basis). A Hamiltonian matrix $\mathbf{H}$ is called s^*-compressible if for each $q \in \mathbb{N}$ an approximate matrix $\mathbf{H}_q$ can be constructed, that has in each row and column at most $O(2^q)$ non vanishing entries and satisfies $\|\mathbf{H} - \mathbf{H}_q\| \lesssim 2^{-tq}$ in the spectral norm for any $0 < t < s^*$. Obviously, the s^*-compressibility of the Galerkin discretization of a certain operator also depends on the specific properties of the basis set. A similar consideration holds for the approximation spaces $\mathcal{A}^s$: The approximation properties of a given basis set can be characterized in terms of a constant $\bar{s}$, and if $s \geq \bar{s}$ the spaces $\mathcal{A}^s$ are essentially empty. Therefore, $\bar{s} \leq s^*$ is a necessary condition in order to fully benefit from the best N-term approximation rate.
(c) Maintaining sparsity: Even if (quasi-)sparse matrices (b) are used in the algorithm, the support of sparse iterates (a) may get bigger by each matrix-vector multiplication, in turn increasing the number of operations needed for the next iteration step. To keep iterates sparse, a $\mathcal{O}(\mathrm{supp}(\mathbf{x}^{(n)}))$ thresholding procedure based on binary binning [28] may be utilized, corresponding to step (3) in algorithm (II).

It is the purpose of our work to investigate the various aspects mentioned in (i) and (ii) for some standard algorithms used in quantum chemistry. Considered together, it enables the design of quasi-optimal algorithms, i.e. algorithms which up to a fixed constant use the minimal

number N of non-null coefficients needed for a prescribed target accuracy ε (determined via (2.7) by the best-N-term approximation), while their computational complexity scales linearly with N.

3 Adaptive correlation methods

Adaptivity in quantum chemical correlation methods, i.e., the selection of important excitation amplitudes, is either based on screening procedures using perturbative arguments or uses locality criteria together with local basis functions. Typical examples for the first approach are canonical orbital based methods like CIPSI [10, 11, 12] or [16, 17] and selective MR-CI methods [13, 14, 15]. The second approach is represented by the local correlation methods of Werner and coworkers [19, 22] or by the work of Ayala and Scuseria [20, 21]. A combination of both approaches is the selective and local CC method of Auer and Nooijen [18]. In the first part of this section, we give for the conceptually simple case of CI a concrete prototype example for a mathematically rigorous adaptive algorithm which uses a residual-based selection criterion and is quasi-optimal in the sense discussed before. Turning to the CC equations, we summarize our recent results about their convergence behaviour and present some preliminary numerical results for an adaptive CC algorithm. Finally, we discuss best-N-term approximation theory for pair-correlation methods.

3.1 A prototype quasi-optimal CI algorithm

For the CI method, corresponding to a Galerkin approach for the Hamiltonian H, we devised in [29] an adaptive algorithm for the computation of the ground state wave function. The basic algorithm (I) is in this case a Richardson/preconditioned gradient eigensolver in which

$$\Delta \mathbf{x}^{(n)} = -\alpha \mathbf{F}^{-1}(\mathbf{H}\mathbf{x}^{(n)} - E^{(n)}\mathbf{x}^{(n)})$$

with a fixed parameter α. In the discrete case, convergence results are well known, cf. Ref. [31]. We considered the case of an infinite dimensional function space with iterates $\Phi^{(n)}$. For this we proved that linear convergence (2.1) is guaranteed in a neighbourhood of the solution. Furthermore, we showed that this result is retained in the sense of (2.2) with the use of approximate applications $APPLY(H, \Phi^{(n)}, \varepsilon)$ of the Hamiltonian, cf. step (2) of Algorithm II. The accuracy ε of the operator application is herein in each step proportional to the size of (an approximation of) the current residual. In [30], we have also extended the following sharp result [31] about the convergence of eigenvalues to our adaptive algorithm:

Theorem 1. *Let $\Phi \in H^1(\mathbb{R}^{3N})$, $||\Phi||_{L_2} = 1$, such that the associated Rayleigh quotient $E = \langle H\Phi, \Phi\rangle$ lies between the k-th and $(k+1)$-th eigenvalue of H, $E_k \leq E < E_{k+1}$ below the essential spectrum of H. Denote*

by

$$\|\Phi\|_{\mathfrak{H}} := \langle (H+\mu I)\Phi, \Phi\rangle^{\frac{1}{2}}, \quad \|\phi\|_{\mathfrak{H}^{-1}} := \langle (H+\mu I)^{-1}\phi, \phi\rangle^{\frac{1}{2}}$$

the norms induced by the shifted Hamiltonian for $\Phi \in H^1$ *and* $\phi \in H^{-1}$*, respectively. Let the shifted Fock matrix be scaled such that*

$$\|I - \alpha F^{-1} H\|_{\mathfrak{H}} \leq \gamma_P < 1. \tag{3.1}$$

If we bound the error in the operator application by

$$||H\Phi - APPLY(H, \Phi, \varepsilon)||_{\mathfrak{H}^{-1}} \quad \leq \quad \gamma_\xi \|H\Phi - \lambda E\Phi\|_{\mathfrak{H}^{-1}},$$

where $\gamma = \gamma_P + \gamma_\xi < 1$*, and obtain the next (inexact) iterate by normalizing*

$$\Phi' = \Phi - \alpha F^{-1}(APPLY(H, \Phi, \varepsilon)), \tag{3.2}$$

there holds for the associated energy $E' = \langle H\Phi', \Phi'\rangle / \langle \Phi', \Phi'\rangle$ *either* $E' < E_k$ *or* $E_k \leq E' < E_{k+1}$*. In the latter case,*

$$\frac{E' - E_k}{E_{k+1} - E'} \leq q^2(\gamma, E_k, E_{k+1}) \frac{E - E_k}{E_{k+1} - E}.$$

Herein, the reduction factor $q < 1$ *depends only on the eigenvalue gap* E_k/E_{k+1} *and the quality (3.1) of the shifted Fock matrix as preconditioner.*

A reliable and accurate estimator for the (in principle infinite dimensional) residual $H\Phi - \lambda E\Phi$ has been designed in Ref. [30]. This estimator thus provides lower and upper bounds for the error of the iterates. The main achievement of our work [29] is a complexity analysis for a concrete realization $MINIEIG(\mathbf{H}, \mathbf{F}, \varepsilon)$ of the adaptive algorithm (II) that shows asymptotically optimal complexity in the following sense:

Theorem 2. *Assume that for a chosen basis* B*, the Galerkin matrices* $\mathbf{H}$ *and* $\mathbf{F}$ *are* s^**-compressible for some* $s^* > 0$ *and that (3.1) holds. Denote the exact ground state solution by* (Ψ, E_0)*, the coordinate vector of* Ψ *by* $\mathbf{u}$ *and by* $P_{\mathbf{u}}$ *the projector on span*$\{\mathbf{u}\}$*. Then for any target accuracy* $\varepsilon > 0$*, the scheme* $MINIEIG(\mathbf{H}, \mathbf{F}, \varepsilon)$*, consisting of the update step (3.2) and a thresholding procedure to coarse the iterates (see* [29]*), produces after finitely many steps an approximate coefficient vector/energy pair* $(\mathbf{x}(\varepsilon), E(\varepsilon))$ *satisfying*

$$\|(I - P_{\mathbf{u}})\mathbf{x}(\varepsilon))\|_{\ell_2} \leq \varepsilon, \qquad |E_0 - E(\varepsilon)| \leq \varepsilon, \tag{3.3}$$

where $I - P_{\mathbf{u}}$ *is the projector on the orthogonal complement of* $\mathbf{u}$*. Moreover, if* $\mathbf{u} \in \mathcal{A}^s$ *for some* $s < s^*$*, then one has for the overall computational and storage requirements*

$$\#\text{flops}\, \mathbf{x}(\varepsilon), \#\,\text{supp}\ \mathbf{x}(\varepsilon) \quad \leq \quad C \cdot (||\mathbf{u}||_{\mathcal{A}^s}/\varepsilon)^{1/s} \tag{3.4}$$

and $||\mathbf{x}(\varepsilon)||_{\mathcal{A}^s} \leq C \cdot ||\mathbf{u}||_{\mathcal{A}^s}$*, where the constants are independent of* ε *and* $\mathbf{u}$ *but depend only on* s *when* s *approaches* s^**, so that* $MINIEIG$ *is an asymptotically quasi-optimal algorithm is the discussed sense.*

The s^*-compressibility of the Fock operator F has been studied in Ref. [32]. Our main result is briefly discussed in Section 4.2 together with the best N-term approximation of orbitals. For the Hamiltonian H we can establish s^*-compressibility, however, this result is presumably not optimal and a more refined analysis is required.

3.2 Convergence of the CC equations

We consider the linked CC formulation in canonical molecular obitals with the HF reference determinant Ψ_0 and excitation operators of the form $T = \sum_{\nu\in\mathcal{J}} t_\nu X_\nu$, where e.g. the twofold excitations, $X_\mu = a_r^\dagger a_s^\dagger a_l a_k$, are indexed by $\mu \simeq \binom{l,k}{r,s} \in \mathcal{J}$. They are given by

$$f_\mu(\mathbf{t}) = \langle \Psi_\mu, e^{-T} H e^T \Psi_0\rangle = \epsilon_\mu t_\mu + \langle \Psi_\mu, e^{-\sum t_\nu X_\nu} U e^{\sum t_\nu X_\nu}\, \Psi_0\rangle \;=\; 0, \tag{3.5}$$

where ϵ_μ stems from the shifted Fock operator

$$\mathbf{F} = \big(\langle \Psi_\nu, [\mathcal{F}, X_\mu]\Psi_0\rangle\big)_{\nu,\mu\in\mathcal{J}} = \mathrm{diag}(\epsilon_\mu)$$

and

$$\mathbf{g}(\mathbf{t}) = \Big(\langle \Psi_\mu, e^{-\sum t_\nu X_\nu} U e^{\sum t_\nu X_\nu}\, \Psi_0\rangle\Big)_{\nu,\mu\in\mathcal{J}}$$

is the corresponding fluctuation potential.

It is shown in [33] that the projected CC equation admits a solution provided that the reference determinant is sufficiently closed to an exact non-degenerate wave function Ψ, and that it allows for a quasi-optimal error estimate. Herein, the error is not estimated with respect to the L_2 norm, but rather in an non-equivalent energy norm. In terms of the unknown amplitudes, this norm can be expressed by

$$\|\mathbf{t}\|_V^2 := \sum_{\mu,\nu\in\mathcal{J}} t_\mu t_\nu \langle \Psi_\nu, [\mathcal{F}, X_\mu]\Psi_0\rangle = \sum_\mu \epsilon_\mu |t_\mu|^2 \,. \tag{3.6}$$

This result is established by proving *strong monotonicity* of the unlinked coupled cluster formulation, which under reasonable conditons provides the same solution (see [33]). Strong monotonicity for $\mathbf{f}$ means that there is a constant $\gamma > 0$ for which

$$\langle \mathbf{f}(\mathbf{v}) - \mathbf{f}(\mathbf{w}), \mathbf{v} - \mathbf{w}\rangle \geq \gamma \|\mathbf{v} - \mathbf{w}\|_V^2 \quad \text{for all} \quad \mathbf{v}, \mathbf{w} \in V \tag{3.7}$$

For a Lipschitz continuous strongly monotone function $\mathbf{f}$, it is known that there exists a damping factor $0 < \alpha \leq 1$ such that the damped quasi-Newton method

$$\mathbf{t}^{n+1} := \mathbf{t}^n - \; \alpha \mathbf{F}^{-1} \mathbf{g}(\mathbf{t}^n), \tag{3.8}$$

converges linearly. Usually, this iteration is used with $\alpha = 1$, obtaining a single Picard fixed point iteration. For this scheme, linear convergence is guaranteed under the more restrictive contraction assumption $\|\mathbf{g}(\mathbf{t})\|_V \leq$

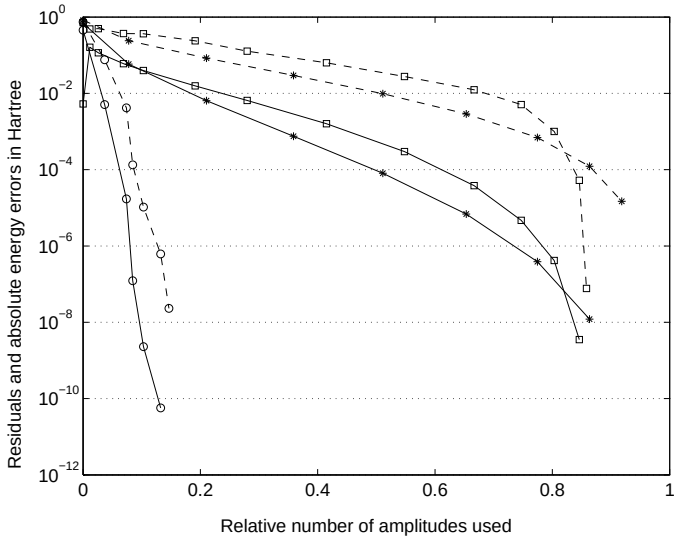

Figure 3.1: *Absolute error in energy (solid line) and residuals (dashed line) during the iteration of the ACC algorithm plotted against the ratio* $N_{coa}/(N_{occ}^2 N_{virt}^2)$ *of selected* T_2 *amplitudes. Results are shown for* H_2O *(aug-cc-pVTZ,* $\square$*),* N_2 *(cc-pVQZ,* $\circ$*) and glycine (Dunning-TZ,* $*$*). Each symbol represents an outer iteration step of the ACC algorithm.*

$q\|\mathbf{t}\|_V$ with a contraction rate $0 < q < 1$. If the convergence of this scheme fails the damped variant is applied instead. We would like to highlight that convergence can be improved by subspace acceleration techniques like DIIS [34].

Improved error bounds for the energy can be provided by consideration of the variational CC Lagrangian

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

with a Lagrange-multiplier $\mathbf{a} \in V$, see [33, 34] for further details. So far, we have not exploited the potential of the duality approach, which from the perspective of accuracy can be seen as an improvement of perturbation techniques. Essentially, the iteration scheme for the CC equations is quite similar to the one for the CI approach.

3.3 Adaptive CC algorithms

We have modified the fixed point algorithm (3.8), which is commonly used in CC algorithms, into an adaptive algorithm in the style of Algorithm II:

Adaptive CC Algorithm (ACC)

Initial iterate: $\mathbf{t}^{(0)} = \mathbf{0}$*, initial accuracies:* $\epsilon_0, \bar{\epsilon}_0$.
for $n = 0, 1, \ldots$ *until convergence do*
(1)$\Delta_{\epsilon_n}\mathbf{t}^{(n)} = APPLY\ (\mathbf{t}^{(n)}, \mathbf{F}^{-1}\mathbf{g}, \epsilon_n)$
(2) *Update* $\overline{\mathbf{t}}^{(n+1)} = \mathbf{t}^{(n)} + \Delta_{\epsilon_n}\mathbf{t}^{(n)}$.
(3) $\mathbf{t}^{(n+1)} = COARSE(\overline{\mathbf{t}}^{(n+1)}, \bar{\epsilon}_k)$.
(4) *Choose* $\epsilon_{n+1}, \bar{\epsilon}_{n+1}$ *proportional to current residual; continue until residual is of desired accuracy.*
endfor

Herein, the evaluation of the fixed point residual $\Delta\mathbf{t}^{(n)} = \mathbf{r}^{(n)} = \mathbf{F}^{-1}\mathbf{g}(\mathbf{t}^{(n)})$ is replaced by the routine $APPLY(\mathbf{t}^{(n)}, \epsilon_n)$ which determines $\mathbf{r}^{(n)}$ up to accuracy ϵ_n. Afterwards, a thresholding step $COARSE(\mathbf{t}^{(n)}, \bar{\epsilon}_n)$ outputs an $\bar{\epsilon}$-approximation $\mathbf{t}_{n+1}$ of $\mathbf{t}$ having a quasi-minimal number of non-null entries to keep the amplitude vector as sparse as possible. On the selected amplitudes produced in this way, we iterated the CC equations 3-5 times before calculating the next full residual. For an iterate $\mathbf{t}$ with support of size N_{coa} instead of the full set of $N_{occ}^2 N_{virt}^2$ amplitudes, the complexity of the matrix-vector multiplications involved in the evaluation of the full CC function is thus reduced by a factor $N_{coa}/(N_{occ}^2 N_{virt}^2)$; for example, the computationally most demanding term in CCSD scales as $N_{coa}N_{virt}^2$ instead of $N_{occ}^2 N_{virt}^4$.
We implemented an adaptive CCSD algorithm based on the NWChem package [35, 36], in which the residual is first calculated exactly and coarsened subsequently, corresponding to a selection of most significant excitation amplitudes in a large basis set. Motivated by considerations common in finite element methods, we investigated if the dual norm $\rho = ||\mathbf{f}(\mathbf{t})||_{\mathbf{F}^{-1}}$ of the residual $\mathbf{f}(\mathbf{t})$ (see Appendix A) may be utilized as an error estimator. In Figure 3.1, the convergence of the adaptive algorithm and the relation between the amount of single and double amplitudes $\mathbf{t}_\epsilon$ and the accuracy of the energy is exemplified for some molecules using canonical orbital bases. The current coarsening threshold ϵ_n was chosen proportional to ρ in each iteration step. Note that although only a part of the amplitudes, predicted by the residual, is used, we have in principle a smooth convergence to the full limit. In the canonical orbital basis, the computational work to be done is reduced only moderately to about 60%, a saving that is of course offset by the extra effort needed for the coarsening step (although in our calculations, further savings result for N_2 from additional symmetries not exploited in NWChem). The more promising case of localized orbitals will be studied in the near future in cooperation with A. Auer. Although our calculations are so far limited to the CCSD approach, it is in principle possible and desirable to include contributions of higher excitations.

3.4 Best N-term approximation for pair correlations

We have also studied the best N-term approximation of pair-correlation functions which appear in the continuous formulation of perturbation the-

ory [37] and in the Jastrow factors [38, 39] used in *quantum Monte Carlo* (QMC) calculations. In order to apply best N-term approximation theory we have to assume an asymptotic smoothness property in a neighbourhood of the electron-electron cusp.

Assumption 1. *The two-particle correlation function* $\tau^{(2)}$ *belongs to* $C^\infty(\mathbb{R}^3 \times \mathbb{R}^3 \setminus D)$*, with* $D := \{(\mathbf{x}, \mathbf{y}) \in \mathbb{R}^3 \times \mathbb{R}^3 : \mathbf{x} = \mathbf{y}\}$*. Furthermore it satisfies the asymptotic smoothness property*

$$|\partial_{\mathbf{x}}^{\alpha} \partial_{\mathbf{y}}^{\beta} \tau^{(2)}(\mathbf{x}, \mathbf{y})| \leq c_{\alpha,\beta} \, |\mathbf{x} - \mathbf{y}|^{1-|\alpha|-|\beta|}, \tag{3.9}$$

for $\mathbf{x} \neq \mathbf{y}$ *and* $|\alpha|+|\beta| \geq 1$*, in any bounded neighbourhood* $\Omega \times \Omega \subset \mathbb{R}^3 \times \mathbb{R}^3$*.*

Here we have used the standard short-hand notation for mixed partial derivatives

$$\partial^{\beta} := \frac{\partial^{\beta_1}}{\partial x_1^{\beta_1}} \frac{\partial^{\beta_2}}{\partial x_2^{\beta_2}} \frac{\partial^{\beta_3}}{\partial x_3^{\beta_3}}, \tag{3.10}$$

with absolute value of the multi-index $|\beta| := \beta_1 + \beta_2 + \beta_3$. A rigorous justification of our assumption is presently under investigation, however, it is obviously satisfied by the standard Jastrow factors employed in QMC calculations [38, 39] and by the r_{12} terms used in explicitly correlated methods [40]. With our regularity assumption we obtained the following lemma, cf., Ref. [41].

Lemma 1. *Suppose* $\tau^{(2)}$ *satisfies Assumption 1. Then* $\tau^{(2)}$ *belongs to* $A_q^{\alpha}(H^1(\Omega \times \Omega))$ *for* $\alpha < \frac{1}{2}$ *and* $\frac{1}{q} = \alpha + \frac{1}{2}$*.*

It has been actually shown that this lemma remains valid under a more realistic assumption which contains contributions from electron-nuclear and electron-electron-nuclear cusps which appear in the Fock expansion and in Hylleraas CI calculations [42].

Because Lemma 1 does not hold for $\alpha \geq \frac{1}{2}$ for any physically reasonable $\tau^{(2)}$, cf. [41], it is only possible to achieve a convergence rate $\sigma_N(\tau^{(2)}) \sim N^{-1/2+\epsilon}$, for any $\epsilon > 0$, with respect to the norm of the Sobolev space $H^1(\Omega \times \Omega)$. This means that the energy converges with $O(N^{-1+\epsilon})$ which is twice the convergence rate that can be achieved with standard pair-correlation methods, like CISD or CCSD, in combination with VXZ-GTO basis sets [43, 44].

4 Adaptive HF and DFT algorithms

In HF and KS theory, we are faced with nonlinear eigenvalue equations

$$F_{\Psi}^{HF} \psi_i = \lambda_i \psi_i, \text{ resp. } F_{\Psi}^{KS} \psi_i = \lambda_i \psi_i, \quad \lambda_i \in \mathbb{R}, \quad i = 1, \ldots, N, \tag{4.1}$$

for an orthonormal set $\Psi = (\psi_1, \ldots, \psi_N)$ of single particle wave functions $\psi_i(\mathbf{x}) \in V$, where $V = H^1(\Omega)$ is the space of one time weakly differentiable functions on $\Omega = \mathbb{R}^3$ for closed shell models and $\Omega = \mathbb{R}^3 \times \{\pm\frac{1}{2}\}$ otherwise, see Appendix A.

4.1 Convergence of the direct minimization algorithm

The Fock operator F_Ψ^{HF} and the Kohn-Sham operator F_ψ^{KS} in (4.1) are derived from the first order conditions for a minimum of the associated energy functionals $\mathcal{J}_{HF}(\Phi)$, $\mathcal{J}_{KS}(\Phi)$, see e.g. [34]. Therefore, instead of solving the eigenvalue equations (4.1), it is also possible to consider HF and KS methods from the minimization point of view, cf. Ref. [45]. In [46] we treated these methods as a classical optimization task of minimizing a functional $\mathcal{J} : V^N \to \mathbb{R}$ under orthogonality constraints, which may be tackled by direct minimization algorithms like the following one:

Projected Gradient Descent Algorithm (PGD)

Require: *Initial iterate* $\Phi^{(0)} \in V$*;*
evaluation of $F_{\Phi^{(n)}}\Phi^{(n)}$ *and of preconditioner(s)* B_n^{-1}
(see comments below)

Iteration:

for $n = 0, 1, \ldots$ *do*

(1) *Compute* $F_{\Phi^{(n)}}\varphi_i^{(n)}$, $i = 1, \ldots, N$.

(2) *Update* $(\lambda_{i,j})_{i,j=1}^N = \langle F_{\Phi^{(n)}}\varphi_i^{(n)}, \varphi_j^{(n)}\rangle \in \mathbb{R}^{N\times N}$.

(3) *Let* $\hat{\varphi}_i^{(n+1)} := \varphi_i^{(n)} - \alpha B_n^{-1}(F_{\Phi^{(n)}}\varphi_i^{(n)} - \sum_{j=1}^N \lambda_{i,j}\varphi_j^{(n)})$.

(4) *Compute orthonormal set* $\Phi^{(n+1)} = (\varphi^{(n+1)})_{i=1}^N$ *for which*
span $\Phi^{(n+1)}$ =*span*$\{\hat{\varphi}_i^{(n+1)} | i = 1, \ldots, N\}$ *(see comments below).*

endfor

The algorithm PGD is implemented in the recent wavelet-basis-based density functional code bigDFT [47], which itself is a part of the open source ABINIT package [48, 49, 50, 51]. Computations show that the convergence of the algorithm is quite robust, also if the HOMO-LUMO gap is relatively small [51]. For implementation of the PGD algorithm, the choice of preconditioners $B_n : V \to V'$ is crucial; see [46] for various possibilities. This is reflected in the theoretical requirements that B_n has to be an elliptic symmetric operator $B_n : V \to V'$, which induces a norm on H^1 that is equivalent to that induced by F^{HF} or F^{KS}; for example, one can use approximations of the shifted Laplacian, i.e., $B_n \approx \alpha(-\frac{1}{2}\Delta + C)$, the choice also taken in the BigDFT project. As regards the orthogonalization of $\widehat{\varphi}_i, i = 1, \ldots, N$, required in step (4), there are various favorable possibilities [46]; nevertheless, it provides the computational bottleneck in nowadays direct minimization HF/DFT computations [51]. For this PGD algorithm, we investigated the questions raised in point (i) of Section 2 and proved the following statements under a certain ellipticity assumption imposed on the Hessian of the respective functional $\mathcal{J}_{HF}(\Phi)$ or $\mathcal{J}_{KS}(\Phi)$, see below.

Linear reduction of the error: We denote by $\mathcal{D}_\Psi$ the L_2-projector on the sought subspace spanned by $\Psi = (\psi_1, \ldots, \psi_N)$. A measure for the energy error of an iterate $\Phi^{(n)}$ is given by

$$\|(\mathcal{I} - \mathcal{D}_\Psi)\Phi^{(n)}\|_{V^N}, \tag{4.2}$$

where the norm $||.||_{V^N}$ is equivalent but, depending on the preconditioner, not necessarily identical to the $(H^1)^N$-norm, see Section A. For the first iterate $\Phi^{(0)}$ sufficiently close to Ψ, there is a constant $\chi < 1$ such that

$$||(\mathcal{I} - \mathcal{D}_\Psi)\Phi^{(n+1)}||_{V^N} \quad \leq \quad \chi \cdot ||(\mathcal{I} - \mathcal{D}_\Psi)\Phi^{(n)}||_{V^N}. \tag{4.3}$$

Note that in contrast to this, the *self-consistent-field* (SCF) iteration scheme, another prominent choice in HF and DFT, is faced with convergence problems [52], for the remedy of which advanced techniques have to be invoked to guarantee convergence [53].

Residuals as error estimators: The vector of "subspace residuals"

$$R^{(n)} = (r_1^{(n)}, \ldots, r_N^{(n)}), \quad r_i^{(n)} = F_{\Phi^{(n)}}\phi_i^{(n)} - \sum_{j=1}^{N} \lambda_{i,j}, \phi_j^{(n)},$$

computed in step (3) of the algorithm, also provides an efficient and reliable error estimator in the sense that for the error $||(\mathcal{I} - \mathcal{D}_\Psi)\Phi^{(n)}||_{V^N}$ sufficiently small, there are constants $c, C > 0$ such that

$$c||R^{(n)}||_{(V^N)'} \quad \leq \quad ||(\mathcal{I} - \mathcal{D}_\Psi)\Phi^{(n)}||_{V^N} \quad \leq \quad C||R^{(n)}||_{(V^N)'}. \tag{4.4}$$

Herein, $||.||_{(V^N)'}$ is the dual norm (see Appendix A) that is equivalent to the norm on V^N only in the discrete case.

Quadratic convergence of the energy: If the orthogonality constraints are satisfied and the functional is two times continuously differentiable, the error in the energy depends quadratically on the approximation error of the minimizer Ψ, i.e.,

$$\mathcal{J}(\Phi) - \mathcal{J}(\Psi) \quad \lesssim \quad \|(I - \mathcal{D}_\Psi)\Phi^{(n)}\|_{V^N}^2 \ . \tag{4.5}$$

The differentiability condition is verified for HF since it depends polynomially on Φ. For DFT, the exchange correlation potential is not known exactly, so the question remains open for the general case.

The previous results apply to the continuous space $V = H^1(\mathbb{R}^3)$ as well as to V standing for a corresponding finite dimensional ansatz subspace of H^1, independent of discretization parameters like the size of the basis set. The mentioned ellipticity assumption for the Hessian of $\mathcal{J}$ under which our results hold is related with fundamental questions like uniqueness of a solution up to unitary transformations; for a simplified linearized HF model, it may be guaranteed if a HOMO-LUMO gap exists, see [46]. Although this assumption in our work cannot be verified rigorously, the proposed convergence behavior is observed by all benchmark computations. Note also that since the PGD algorithm is gradient directed, a line search based on the Armijo rule will guarantee convergence in principle, even without a coercivity condition [54, 55].

4.2 Best N-term approximation for HF orbitals

The HF equation is of outstanding significance in electronic structure calculations. It is therefore remarkable that almost no rigorous results were known about the approximation properties of the solutions, the so-called HF orbitals. It is only known for the H atom [56, 57] that GTO bases provide almost exponential convergence and there exists merely numerical evidence [58] that this result extends to general atoms and molecules. We have studied best N-term approximation spaces for HF orbitals and the corresponding one-electron reduced density matrix. More precisely, our results uses the level-shifting algorithm. According to the analysis of Cancès and Le Bris [53], this SCF iteration scheme converges and therefore satisfies our requirement (i) for an adaptive algorithm. The corresponding iterates and the final SCF solutions are smooth except at the nuclei. In order to apply best N-term approximation theory we require all intermediate and final solutions to be *asymptotically smooth* in a neighbourhood of a nucleus, i.e.,

$$|\partial_{\mathbf{x}}^{\beta}\phi_n(\mathbf{x})| \leq C_\beta |\mathbf{x}-\mathbf{A}_k|^{1-|\beta|}, \text{for } \mathbf{x} \neq \mathbf{A}_k, \quad \text{and } |\beta| \geq 1. \tag{4.6}$$

The asymptotic smoothness property essentially means that we get control on the partial derivatives of the orbitals near the nuclei. It is an immediate consequence of the following theorem [59]:

Theorem 3. *All intermediate iterative solutions* $\{\phi_n^{(i)}\}_{n=1,\ldots,N/2}$ *as well as the final SCF solutions* $\{\phi_n\}_{n=1,\ldots,N/2}$ *of the closed-shell HF equations, obtained via the level-shifting algorithm, exhibit Taylor asymptotics (polar coordinates) in a neighbourhood* Ω_k *of any of the* $k = 1, \ldots K$ *nuclei, i.e.,*

$$\phi = \omega(r) \sum_{j=0}^{l-1} c_j(\varphi,\theta) r^j \; + \; \Phi_l,$$

with $\Phi_l \in C_B^m(\Omega_k)$ *for* $l > m$*, provided that the initial guess* $\{\phi_n^{(0)}\}_{n=1,\ldots,N/2}$ *possesses this property. Here* $\omega \in C_0^\infty(\Omega_k)$ *denotes a cut-off function which is equal to 1 in a neighbourhood of the nucleus. Furthermore we have* $\phi \in \mathcal{S}(\mathbb{R}^3 \setminus \cup_{k=1}^K \Omega_k)$*.*

This theorem together with Lemma 1, from Ref. [60] enables general conclusions about the best N-term approximation of HF orbitals and the corresponding one-electron reduced density matrix.

Theorem 4. *The SCF solutions* ϕ_i *from Theorem 3 and the corresponding one-electron reduced density matrix belongs to* $A_q^s(H^1)$ *for each* $s > 0$ *and* $\frac{1}{q} = s + \frac{1}{2}$*.*

Theorem 4 shows that for a sufficiently regular univariate wavelet basis with $p > s+1$ vanishing moments, the orbitals ϕ_i and one-electron reduced

density matrix can be approximated in the corresponding *anisotropic* 3d or 6d tensor product wavelet basis with optimal convergence rate $\sigma_N(\phi) \sim N^{-s}$ with respect to the norm of the Sobolev space H^1. For the corresponding *isotropic* 3d tensor product wavelet basis, the optimal convergence rate reduces to $\sigma_N(\phi) \sim N^{-s/3}$ for the orbitals.

We are now able to compare the best N-term approximation rates with our result for the s^*-compressibility of the discrete Fock operator in an isotropic wavelet basis which satisfies certain Bernstein and Jackson estimates in the Sobolev space $W^t_\infty(\mathbb{R}^3)$, cf. Ref. [32] for further details. It has been shown that the infinite Galerkin matrix of the Fock operator is s^*-compressible with $s^* = t/3$. For example, in the case of spline wavelets of order $d = t + 1$ and with $p \geq t + 1$ vanishing moments we can achieve N-term approximation rates $s < t/3$, i.e., $\bar{s} = t/3$ cf. Section 2 (ii), which nicely fits together with $s^* = t/3$. The factor $1/3$ enters because of the usage of isotropic tensor product wavelet bases. These considerations are necessary but not sufficient to demonstrate that an adaptive wavelet algorithm with optimal computational complexity exists in the sense of Ref. [27].

5 Conclusions

We have presented our program for the numerical analysis of adaptive iterative methods in electronic structure calculations. Key features include the convergence analysis of iterative algorithms, sparse approximations of the final solution and of intermediate iterates, and sparse approximate discretizations of the Hamiltonian. Partial results of this extensive program include adaptive CI and CC methods and a fairly comprehensive study of the Hartree-Fock model. However much remains to be done in order to use our results as a basis for coherent adaptive methods which allow for controllable accuracies and complexity the one hand while they are competitive to already existing adaptive algorithms, based on physical and chemical insights and practical experience, on the other hand.

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A Mathematical concepts and notions

This section is meant to explain some of the mathematical notions fundamentally related with the treatment of the electronic Schrödinger equations from the mathematician's point of view. We refer e.g. to the mono-

graph [61] for a detailed exposition of the subject.

Hilbert space, stable bases: The basic space for electronic structure calculation is some Hilbert space $\mathcal{H} = L_2$ of square integrable functions (in the Lebesgue sense). On this space, a basis B_0 may be chosen, and we may then express every $\Psi \in \mathcal{H}$ by basis functions Φ_i from B_0, $\Psi = \sum c_i \Phi_i$. If the ℓ_2-norm of the coefficient vector $\mathbf{c} = (c_i)$ of the solution then reflects (up to constants) the L_2-norm of the corresponding wave function, i.e.,

$$c \cdot \|\mathbf{c}\|_{\ell_2} \;\leq\; ||\Psi||_{\mathcal{H}} \;\leq\; C \cdot \|\mathbf{c}\|_{\ell_2}, \tag{A.1}$$

with c, C independent of Ψ, B_0 is a so-called *stable* or *Riesz basis*. Note that (A.1) does not need to hold although B_0 is linearly independent; for an orthonormal basis, it is fulfilled as equality, the so-called *Parseval identity*. In general, a relation like in (A.1) between two norms is termed *equivalence of norms*.

Unboundedness, Sobolev space H^1, weak formulation: Operators containing differential operators, as for instance the Hamiltonian or the Fock/KS operator, are unbounded and not defined everywhere on $\mathcal{H}$; this poses some severe formal problems on the one hand, reflecting on the other hand in the fact that the discretized equations get more and more ill-conditioned the bigger the basis set is chosen. The common procedure for a Schrödinger-like equation, say $H\Psi = E\Psi$, is to switch to the *bilinear form* $\langle H\Psi, \Phi\rangle$ associated with H, which is maximally defined on the *Sobolev space* H^1 of functions from $\mathcal{H}$ for which a first derivative exists (in the weak sense) and is in L_2, that is, $\Psi \in H^1$ iff the norm

$$||\Psi||_{H^1} = \left(\int |\Psi(x)|^2 dx \;+\; \int |\nabla\Psi(x)|^2 dx \right)^{\frac{1}{2}}$$

(which is not equivalent to the L_2 norm) stays finite. The equation then is treated in the weak formulation

$$\langle H\Psi, \Phi\rangle = E\langle \Psi, \Phi\rangle \;\text{ for all }\; \Phi \in B_1, \tag{A.2}$$

where B_1 is a basis in the restricted ansatz space H^1. Choosing a basis B_1 which is stable with respect to H^1, i.e. (A.1) holds with the H^1-norm instead of the L_2-norm, enables an estimate of the H^1-norm of the iterates from the ℓ_2-norm of their coefficient vector.

An interesting fact is that in many cases, the norm associated to the shifted energy $\|\Psi\|_{\mathfrak{H}} = \langle (H + \mu I)\Psi, \Psi\rangle^{1/2}$ is actually equivalent to the H^1-norm. We therefore often have a relation between the error of the iterates, measured in the H^1-norm, and the error of the energy (which often is quadratic, see e.g. (4.5) and analogous results from [29] for CI). Note that in contrast, no such equivalence holds for the L_2/ℓ_2 norms from (A.1), rendering the coefficients of Ψ in an L_2-basis useless for error estimation, especially when the basis sets get large.

Dual norms, Sobolev space H^{-1}, residual estimators: In the above

setting, the operator of interest, say H, can be viewed as an operator assigning to an element $\Psi \in H^1$ the linear functional $\psi : f \mapsto \langle H\Psi, f\rangle$. H is therefore mapping to the *dual space* H^{-1} of H^1, i.e., the space of continuous linear functionals acting on H^1. An important consequence of this is that the residual, say $r = H\Psi - E\Psi$, is an element of H^{-1} and has to be measured in a corresponding norm. This may be done by taking the norm $||r||_{A^{-1}} := \langle A^{-1}r, r\rangle^{1/2}$ where A is a bounded, strictly positive operator mapping $H^1 \to H^{-1}$. A typical choice is for example the shifted Laplacian Δ or the shifted Fock operator F. In this norm it is often possible to obtain an equivalence to the H^1-error of the iterates which often provides in turn a reliable and efficient estimator for the error in energy.

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