



Franz Michael Dolg (Ed.)

Progress in Physical Chemistry Volume 3

Modern and Universal First-principles Methods for
Many-electron Systems in Chemistry and Physics

Oldenbourg



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Modern and Universal First-principles Methods for
Many-electron Systems in Chemistry and Physics

by
Franz Michael Dolg (Ed.)

Series Editor: Helmut Baumgärtel

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Like all natural sciences Physical Chemistry also is strongly affected by a development which leads to an inflation of information details which cannot be thoroughly covered in its depth by the regular journal world. Therefore the editors and the publisher of Zeitschrift für Physikalische Chemie have decided to provide a platform for scientists to present their research and results on a broader basis. Thus the book series "Progress in Physical Chemistry" has been created.

The first volume of the series is devoted to "Different Aspects of Intermolecular Interaction". It collects most important reviews on the topic published in Zeitschrift für Physikalische Chemie between 2004 and 2006.

Volume 2 covers the results of the Collaborative Research Center (SFB) 277 of the German Research Foundation (DFG).

Volume 3 covers the results for the Priority Programm (SPP) 1145 of the German Research Foundation (DFG).

Helmut Baumgärtel
(Series Editor)

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Preface

Volume 3 of the series 'Progress in Physical Chemistry' comprises 27 articles reporting method developments in the field of first-principles electronic structure theory in chemistry and physics. These papers, most of them with review character, have all been written by members of the German-wide Scientific Priority Program (SPP) 1145 'Modern and Universal First-principles Methods for Many-electron Systems in Chemistry and Physics' of the German Research Foundation (DFG). The SPP 1145 was funded by the DFG during three project periods from 2003 to 2010 and brought together scientists from theoretical chemistry, theoretical physics and applied mathematics. All contributions have also been published in a special topical issue of 'Zeitschrift für Physikalische Chemie' (2010/03–04).

During the last symposium of the former DFG SPP 'Relativistic Effects in Heavy-Element Chemistry and Physics' (1994–2000, coordinator Bernd A. Hess†) in 2000 at Kloster Banz a small group of scientists, among them e.g. Werner Kutzelnigg, decided that it should be attempted to initiate a new purely theoretical priority program in the field of electronic structure theory. After dealing intensively and very successfully for six years within the ending priority program with the development of efficient and accurate approaches for the evaluation of relativistic contributions in first-principles calculations in chemistry and physics, it was decided that the emphasis of the new priority program should be on method development for the many-electron problem, i.e. mainly on electron correlation. The honor of writing the actual proposal to the DFG was left to a task force of, at that time, younger scientists (Eberhard Engel, Heinz-Jürgen Flad as well as the author), who assembled the contributions from numerous colleagues from theoretical chemistry, theoretical physics and applied mathematics in an application. Later, in 2002 the DFG granted funding of the SPP 1145 and after the initial symposium 2003 in Bonn 27 research projects were launched. For the second and third term 26 and 24 projects were granted in 2005 and 2007, respectively. The DFG funding consisted mainly in PhD student positions and a few postdoctoral positions for the participating research groups, funds for traveling and for holding yearly symposia for the entire SPP 1145 community as well as workshops on special topics.

The main idea of the SPP 1145 was to serve as a common platform for scientists from the various usually disjunct communities focussing on first-principles electronic structure calculations. It was especially intended to lead to an intense exchange of ideas between the method developers. The followers of density functional theory should learn from those of *ab initio* wavefunction theory

and *vice versa*, and both communities should get in closer contact to mathematicians interested in the field. The range of applicability of existing approaches should be extended, their accuracy should be increased. Besides this less frequently applied as well as new methods should be further developed within the priority program. The contributions to this volume highlight various exciting theoretical developments in line with these intentions which were, at least in part, inspired and made possible by the SPP 1145.

The contributors of this volume thank the reviewers for their valuable comments and the editorial staff of *Zeitschrift für Physikalische Chemie* for their helpful support. The present and former members of the SPP 1145 are grateful to the DFG for the generous funding of a theory-only program. They acknowledge the continuous interest, administrative advice and professional guidance by the DFG representatives Drs. Johanna Kowol-Santen and Frank-Dieter Kuchta. Special thanks are due to the members of the international review panels who did spend a lot of their precious time to review the applications, read the reports and select the projects to be funded. Their presence at the SPP 1145 symposia was highly appreciated and had without doubt positive effects on the program as a whole as well as on many of the projects refereed by them.

Finally, as a coordinator and spokesman I would like to thank my colleagues in the SPP 1145 steering group, i.e. Profs. Hubert Erbert, Jürgen Gauß, Andreas Görling, Eberhard Groß, Bernd Hess†, Willem Klopper, Hans-Joachim Werner and Priv.-Doz. Eberhard Engel, as well as Dr. Heinz-Jürgen Flad for their work initiating the SPP 1145 and making it successful. Last but not least I thank all authors of the present volume for their contributions and their efforts to provide overviews summarizing for their part of the field six years of exciting research efforts in modern electronic structure theory.

Cologne, March 2010
Michael Dolg

A Critical Evaluation of the Dynamical Thresholding Algorithm in Coupled Cluster Calculations

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Dynamical Thresholding Algorithm / Coupled Cluster Doubles

A new implementation of the Dynamical Thresholding (DT) coupled cluster doubles (CCD) approximation is presented. Using prescreening techniques for the intermediate quantities that occur in the CCD amplitude equations, a computationally efficient algorithm is obtained, in which one single threshold allows for control of accuracy. A critical evaluation of the accuracy and efficiency is carried out for two testcases. Furthermore, the issue of potential energy surface discontinuities and the usage of enveloping localized orbitals is discussed in detail.

1. Introduction

One of the major trends in modern developments of electronic structure theories is the evolution (one can also say the renaissance) of low-scaling correlation methods, that overcome the high computational cost in post-HF ab-initio methods. However, these approaches are only currently being applied to a larger variety of problems, and most of them are not yet used on a routine basis as black-box tools in quantum chemistry. Nevertheless, there is already a wide range of different approaches, of which the most practicable are probably yet to evolve from a longer process of trial and improvement.

One type of approximation follows from applying the early ideas of integral screening to the the wavefunction parameters that are expressed in a local basis. A screening scheme is then constructed for the amplitudes or coefficients which indirectly leads to a reduction of computational effort due to the sparsity in the parameters and integrals. [1–9] As a related ansatz one could also also count

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newer schemes in the framework of the coupled electron pair approximation based on pair natural orbitals (PNOs), in which a cutoff for the PNOs is used to screen wavefunction parameters [10] or certain implementations of coupled cluster (CC) methods with periodic boundary conditions. [46]

In the most successful type of approximations up to date, often simply referred to as "local methods" [11–17], the occupied and virtual orbitals are localized for example by the Pipek-Mezey (PM) scheme and by constructing projected atomic orbitals (PAOs).[17,19] Prior to the calculation, a limited set of wavefunction parameters is selected either based on distance, overlap or other criteria. Then, the working equations are solved for a subset of index pairs and within limited orbital domains, so that the number of parameters only grows linear with system size by construction. This scheme has been implemented for a wide variety of methods [20–35] and also for the calculation of molecular properties. [36–45]

A further approach to reduce the high computational complexity of post-Hartree-Fock methods, which is conceptually simple yet elegant and somewhat more coarse-grained are schemes in which the system is split into fragments of some kind and energies of fragments and interactions between fragments are calculated until the total energy converges. This includes incremental incremental methods [48–52] such as the "local ansatz" by Stollhoff, Stoll and Fulde [53–58] as well as divide-and-conquer strategies or related schemes for correlated methods. [47,59,60]

While screening based approaches are often associated with higher computational cost and might also suffer from convergence problems, they are expected to be robust and applicable as black-box methods. "Local methods" can be set up extremely efficiently, are fairly robust but suffer from problems due to localization or truncation schemes. [61–64] Incremental or divide-and-conquer approaches can easily be used for periodic systems and in QM/MM or QM/QM hybrid approaches, have the appeal of naturally low scaling and are easy to implement. However, the fact that no closed expression for a wavefunction is available in this case might render the calculation of certain properties difficult.

The Dynamical Thresholding (DT) algorithm is an alternative route to a local approximation for CC methods that falls under the screening-based methods. Here, local energy contributions are calculated at the MP2 level of theory and the size of each contribution is used as a screening criterion for the evaluation of the CC amplitudes. [5] This way, one single threshold can be used to truncate the wavefunction parameters and to go from the full CC treatment to an approximation that in the limit reduces to the MP2 result. The great advantage of this approach is, that no choice of special pairs, excitation domains or a division of the system into subunits are made prior to the calculation. As the truncation of the wavefunction parameters is guided by the MP2 guess it can be regarded as adapted to the system in question and qualifies this approximation as a black-box scheme in which only one parameter, the amplitude threshold, has to be set by the user. First benchmarks from a CCSD pilot implementation of the DT

algorithm that has been devised using the TCE program generator [65–67] within the NWChem program package [68] were very promising. Especially the fact that the resulting error correlates well with the chosen threshold makes this approximation attractive. This scheme allows the user to adjust the threshold in such a way, that sufficient accuracy for a certain application is obtained.

In this contribution we describe the first implementation in which the reduction of the wavefunction parameters within the DT-screening scheme leads to a considerable reduction of computational effort. Furthermore, some fundamental issues for the implementation of the DT-coupled cluster doubles (CCD) approach are discussed like the intermediate problem in local CC implementations, the use of enveloping localized orbitals (ELOs) and potential energy surface discontinuities.

2. The DT-CCD implementation

Before focusing on the motivation for choosing the CCD method for an efficient implementation of the DT algorithm, we would first like to summarize the basic features of the scheme:

- After a HF-SCF calculation has been carried out, the MP2 energy of the system is calculated in the local basis. The current algorithm in principle supports any choice of local basis, ranging from pure atomic orbitals for representing the occupied/virtual space up to the common PM/PAO basis. However, in the following we will be focusing on the ELO/AO combination (for comparison, also the PM/AO combination will be considered). It should be noted, that for optimal performance in matrix multiply operations the local amplitudes are not treated element by element but rather in blocks of amplitudes.

- In the screening step it is decided whether a block of amplitudes is treated at the CC level of theory or approximated by perturbation theory, based on the MP2 energy contributions in the local basis. This way, two sets of amplitudes are obtained - the (optimally very small) set of CC amplitudes (denoted at CC-subset in the following) and the screened amplitudes, that will be termed as PT-subset (perturbative amplitudes) for simplicity in the following.

- For solving this set of hybrid equations, two schemes have been proposed, termed weakly and strongly coupled scheme. For both schemes all contractions in the CC equations are only carried out if the resulting residual corresponds to a block of amplitudes from the CC-subset. The two schemes differ in which set of amplitudes is used in the contractions: In the weakly coupled scheme, only amplitudes from the CC-subset are contracted into residual elements of the CC-subset. In the strongly coupled scheme all amplitudes, from the CC- and PT-subset, are used for the contractions into the CC-subset of the residual. A crucial point is the treatment of the amplitudes in the PT-subset. While one would assume that this part of the amplitudes is fixed during the CC iterations, experience shows that this inevitably leads to convergence problems in solving the hybrid

equations. Preliminary studies have shown that for the DT scheme as described here, this is even the case if strong orthogonality is preserved and is due to the use of nonorthogonal or redundant orbitals for representing the virtual or occupied space in the combined equations. This problem, however, is elevated if an additional set of zeroth order equations is solved for the PT-subset of the amplitudes. For the strongly coupled algorithm, relatively smooth convergence to the exact result is observed, such that a series of calculations might even make extrapolation schemes applicable.

After evaluation of the contractions in the amplitude equations the residual is transformed to the canonical basis, weighted by the denominator and back-transformed to the local basis to proceed to the next iteration (including DIIS convergence acceleration [69]). Detailed equations in the local basis for the CCD method can be found in Appendix A.

This way, an algorithm is obtained in which the screening of the wavefunction parameters is applied to the most expensive terms in the CC equations, with remaining steps for all amplitudes that have low prefactors and scale as N^5 at worse. The back and forth transformation of the local amplitudes might be regarded as inconvenient but compared to other N^5 steps it is comparably cheap and also serves another purpose. By transforming to the MO basis in every iteration the local amplitudes in the ELO/AO basis are projected onto the proper occupied and virtual spaces, which is related to the procedure Werner et al. use for the amplitude update in the LCC scheme. [20]

The aim for a computationally efficient local approximation in the spirit of the DT algorithm is a scheme that reduces the computational effort in the same way as the approximation reduces the number of amplitudes in the CC-subset. But while the number of amplitudes drops rapidly as the threshold is increased, especially for larger systems, the computational effort does not only depend on the number of non-zero t_2 amplitudes and integrals. In order to achieve optimal scaling of the algorithm, the CC equations have to be factorized. [70] In the factorized equations, intermediates occur, for which in principle no sparsity can be assumed. In order to illustrate this, let us consider a term from the t_2 equations which is quadratic in the t_2 amplitudes (for example the sixth term in equation 1 in Appendix A). If this term is factorized, two contractions are obtained as symbolically depicted in Fig. 1. In the first contraction the two-electron integrals are multiplied with the t_2 amplitudes to form an intermediate quantity. In the second contraction the intermediate is multiplied with the t_2 amplitudes to give the final contribution to the residual. For all quantities, the localized basis leads to sparsity in the elements, and for the residual the same sparsity can be assumed as for the amplitudes (it should be noted that in this example, the weakly coupled algorithm is assumed). In the case of a term like this, the first contraction leads to an intermediate that has a sparsity that is not as pronounced as in the original tensors - in the example of Fig. 1 this is illustrated by a simple "multiplication" of the two blocked matrices. If the intermediate is then contracted with the amplitudes into the residual, for which the non-zero blocks are known, several blocks

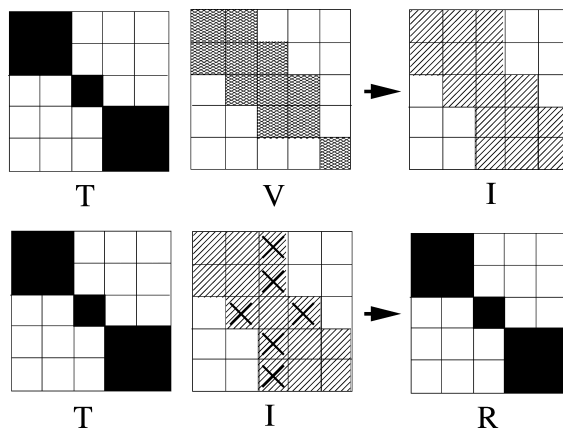


Fig. 1. Symbolic representation for a typical contribution of a CCD t_2 term quadratic in the amplitudes. Filled blocks depict large entries, empty blocks depict entries close to zero. Even if sparsity in the amplitudes (denoted as "T") and integrals (denoted as "V") is assumed, sparsity in the intermediate (denoted as "I") quantity does not automatically follow. If the intermediate is contracted into the residual (denoted as "R", same sparsity as for t_2 is assumed) certain blocks will not be needed that have been formed before (marked with an "x").

that are contained in the intermediate are not needed. Thus, even if the amplitudes and integrals are sparse, this property is lost in the intermediates.

For terms quadratic in the amplitudes a remedy for this is the following prescreening strategy: Before the actual contraction a "dry-run" is carried out at the block level, so that all blocks of the intermediates can be identified that will actually be used in the final contraction. This is easily possible, as in the second contraction the only other quantities are the residual and the amplitudes, for which the block structure is known. However, if a term is more than quadratic in the amplitudes, three or more steps are needed and several contractions will occur in which an intermediate is contracted with amplitudes to form further intermediates. This renders any kind of prescreening difficult if not impossible. While amplitudes and integrals might be sparse, efficiency is then lost in equations that include a hierarchy of intermediates for which there is no pronounced sparsity. A good example are CCSD t_2 terms that are cubic or quartic in t_1 . This problem has been identified relatively early by Scuseria and Ayala who devised an AO-based CC algorithm.[71] Here, the intermediate problem is avoided by choosing Brueckner-CCD [72–74] as a starting point rather than conventional CCSD. This way, no terms have to be treated in which more than one intermediate occurs without having to neglect the influence of single excitations. In order to devise a computationally efficient DT-CC implementation we follow the same path, for simplicity focusing on CCD at first. In a previous publication we have presented a simple scheme for the conversion of the canonical CC equations into the ELO/AO representation.[5] Following this scheme, the CCD equations can easily be written in the local basis as shown in Appendix A.

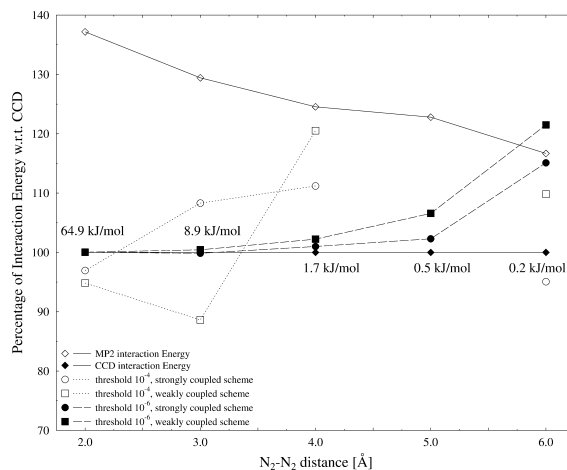


Fig. 2. Truncation error of the correlation contribution to the interaction energy of two N₂ molecules with respect to full CCD. Note that for a threshold of 10⁻⁴ the points for 5 Å have been omitted due to the very large deviations from the CCD and MP2 results.

3. Efficiency benchmark for the DT-CCD algorithm

While previous benchmarks for the DT scheme focused on errors in the absolute energy, the description of chemical reactions or stability of molecular structures requires reliable results of relative energies. Furthermore, a scheme for actual applications has to be computationally efficient, so that a central, though not necessarily the most important point is the reduction of computational effort. As testcase that includes the calculation of energy differences, the N₂-dimer in the side-on configuration, using the aug-cc-pVTZ [75,76] basis set has been chosen.[77] Furthermore, this system can also be viewed as a very simple model for distant, weakly interacting molecular fragments. For two N₂ molecules the correlation contribution to the interaction energy rapidly decreases with distance. At the CCD/aug-cc-pVTZ level of theory it is reduced from about 65 kJ/mol at 2 Å to about 0.2 kJ/mol at 6 Å (see Fig. 2).

As the DT algorithm is designed for a good threshold-error correlation, the error in the interaction energy should also correlate well with the threshold chosen. In the previous work it was found, that a given accuracy in the energy is reached at a threshold of approximately one order of magnitude higher.[5] If mH accuracy is desired, the threshold should be adjusted to around 10⁻⁵. For the N₂ dimer the interaction energy should be reproduced well up to a distance of 2–3 Å at thresholds of 10⁻⁴, thresholds of 10⁻⁶ should yield a good approximation over almost the full range of distances under consideration. If the strength of the interaction drops below the accuracy at the given threshold, the parameters that describe the weak interaction should be screened away and as a consequence the number of amplitudes in the CC-subset should reduce to approximately double the number of one N₂ molecule.

Fig. 2 shows the percentage of the full correlation contribution to the interaction energy for the DT-CCD algorithm with thresholds of 10^{-6} and 10^{-4} as a function of the intermolecular distance.[78] It should be noted that the scale ranges from 70 to 140 %, the zero line being the CCD correlation contribution to the interaction energy. The MP2 result is also given, which systematically overestimates the correlation contribution for the interaction energy. In this calculation, the scheme described in Section 2 has been applied, so that for the weakly coupled algorithm the sparsity information for amplitudes, integrals and the residual is used, while for the strongly coupled algorithm no sparsity information is used for the amplitudes. Before discussing the truncation error with threshold and intermolecular distance it should be mentioned that at a threshold of 10^{-6} the number of amplitudes in the CC-subset is 99 % of the full set of amplitudes at 2 Å, 74 % at 4 Å and drops to 30 % at 6 Å. For a threshold of 10^{-4} it is 86 % at 2 Å, 28 % at 4 Å and drops to about 15 % at 6 Å, which is approximately double the number of amplitudes of one N_2 molecule. Thus, the algorithm performs the desired adaption of the number of wavefunction parameters to the physics of the systems within the limits of the given threshold.

For a threshold of 10^{-6} the strongly and weakly coupled DT schemes reproduce the full CCD result within 10 % up to a distance of 5 Å (note that at this distance 10 % of the correlation contribution is one hundredth of a mH). At 6 Å the results practically reduce to the MP2 value. For a threshold of 10^{-4} it becomes obvious that the error is stable up to about 4 Å, the strongly coupled scheme being somewhat more systematic. However, as the absolute value of the correlation contribution of the interaction energy drops below 1 kJ/mol most of the wavefunction parameters that describe this subtle effect are screened away and the approximation breaks down. Here, very unsystematic results are obtained that are even far from the MP2 values the algorithm ultimately converges to. Naturally, very large thresholds should be avoided, as in this case only very few but large contributions are refined in the CC-subset. The influence and the sign of these cannot be expected to be systematic in any respect.

The crucial point for an accurate yet efficient approximation is the reduction of the computational effort as more and more wavefunction parameters are discarded. Fig. 3 displays the timings for the CCD t_2 contributions in one iteration partitioned into the contributions from the different terms (see Appendix A) at a distance of 5 Å. The bar on the left is the DT algorithm without any truncation in the amplitude equations, the bar on the right is the same scheme for one N_2 molecule multiplied by a factor of two as a reference for the ideal linear scaling limit of two noninteracting systems. The full treatment is actually about a factor of 60 more expensive than the corresponding monomer calculation, which is in good agreement with the theoretical scaling of the CCD method that should yield a factor of 64. It should be noted that this example is still comparably small, so that two terms that scale as N^6 dominate the overall time, rather

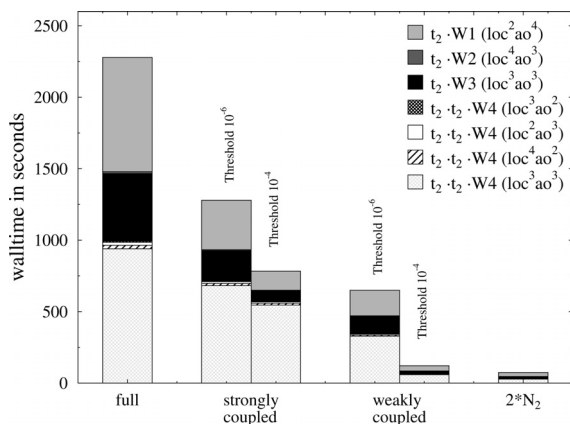


Fig. 3. Walltime in seconds for one CCD t_2 iteration for the N_2 dimer in an aug-cc-pVTZ basis at 5 Å distance. See Appendix A for an explicit formulation of the different CCD terms encoded in the barplot.

than just the particle-particle ladder term (that scales as $\text{occ}^2 \text{virt}^4$) as it is often the case in actual applications. [79]

At a distance of 5 Å and a threshold of 10^{-4} , the weakly coupled algorithm is approximately by a factor of three more expensive than the monomer calculation, which is reasonably close to the optimal behavior. The strongly coupled algorithm exhibits a factor of more than 20 for this threshold, which is due to the lack of sparsity information used for the t_2 amplitudes in the algorithm and applies to practically all terms of the t_2 equations. Thus, while being more robust in terms of truncation error this scheme is by far not as efficient computationally wise, even if weakly interacting systems are regarded.

While the N_2 dimer has been used as a proof of principle for the reduction of the computational effort, the actual scaling of the method with systems size has to be investigated in a more realistic setup. For this purpose we have chosen to investigate a simple alkane chain with increasing length (C_nH_{2n+2} with $n = 2$ to 12) at a threshold of 10^{-4} . [77] While this is a very common type of example - often glycine chains or chains of separate molecules are used - one should keep in mind that this is also a fairly simple testcase, as linear molecules have a more pronounced sparsity of wavefunction parameters than three dimensional structures. For the smallest molecule in this series, the DT algorithm does not screen any amplitudes at all, for C_6H_{14} 19 % are included in the CC-subset and for $C_{12}H_{24}$ only 6 % of the amplitudes are refined at the DT-CCD level of theory. Already starting from C_6H_{14} the additional number of amplitudes in the CC-subset for every further C_2H_4 unit is roughly constant (see second plot in Fig. 4). At the top and at the bottom of Fig. 4 the timings per iteration and the truncation error for the alkane chain using the weakly coupled DT-CCD algorithm (in a 6-31G* basis [80,81]) and a threshold of 10^{-4} are shown. For the largest example,

$C_{12}H_{24}$ the time required for one iteration is reduced by a factor of almost 40. [82] While not scaling linear, the computational scaling is far lower than N^6 - roughly doubling the system size from C_6H_{14} to $C_{12}H_{24}$ yields a factor of about 8 in computational time. The error in terms of absolute energy introduced by choosing a threshold of 10^{-4} is less than a mH for all cases. Nevertheless, it is growing with system size. While the basic construction of the DT algorithm should in principle yield a stable error for a broad variety of systems, this behavior is yet not surprising. On the one hand, as the system grows larger, also the number of screened parameter increases drastically, so that the neglected contributions might sum up to somewhat larger values. On the other hand, as it can be argued for any local method, as the energy is an extensive quantity, so should be the error in the energy made by an approximate scheme. [83] Second from the bottom of Fig. 4 the relative energy for the extension of the molecular chain by a C_2H_4 fragment is shown in order to give an estimate for the accuracy of relative energies. It should be noted that the same scale on the y-axis has been used as for the absolute error plot below. In contrast to the error in the absolute energy the error of the relative energy is stable as the chain is extended. Overall, although this is a fairly simple testcase, the algorithm already shows a remarkable saving of the computational time with truncation errors that are below one mH for absolute and relative energies.

4. Enveloping localized orbitals (ELOs) and the issue of potential energy surface discontinuities

As mentioned before, a new local representation of the occupied orbitals - the ELOs - has been constructed for the usage in the DT scheme. These are a non-orthogonal set of linearly independent orbitals, that are atom centered and thus better localized than for example PM orbitals. Localization beyond occupied space localizability is achieved by mixing in virtual components yielding a set of AO-like orbitals, that are more numerous than the occupied orbitals but far less numerous than the AOs themselves.

The procedure for constructing the ELOs is based on projecting the occupied orbitals on the AOs of a given center and extracting a minimal basis set for each atom. This way, for hydrogen one ELO is obtained, for first row atoms five ELOs are obtained etc. In further steps it is ensured that the set of new orbitals is strictly atom centered and exactly spans the occupied space.

In Fig. 5 four of the five ELOs for carbon are displayed (the fifth one not plotted being the 1s component) for the sp -carbon in carbon monoxide, the sp_2 -carbon in ethene and the sp_3 -carbon in fluoromethane for a cc-pVTZ basis set. [84] For all of these compounds the ELOs are very similar. Each of the ELOs is atom centered and in character mostly AO-like, although for carbon monoxide with a triple bond and a lone electron pair the ELOs do somewhat resemble hybrid orbitals.