Near-exact CCSDT energetics from rank-reduced formalism supplemented by non-iterative corrections

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Abstract

We introduce a non-iterative energy correction, added on top of the rank-reduced coupled-cluster method with single, double, and triple substitutions, that accounts for excitations excluded from the parent triple excitation subspace. The formula for the correction is derived by employing the coupled-cluster Lagrangian formalism with an additional assumption that the parent excitation subspace is closed under the action of the Fock operator. Owing to the rank-reduced form of the triple excitation amplitudes tensor, the computational cost of evaluating the correction scales as $N^7$ with the system size, $N$. The accuracy and computational efficiency of the proposed method is assessed both for total and relative correlation energies. We show that the non-iterative correction can fulfill two separate roles. If an accuracy level of a fraction of kJ/mol is sufficient for a given system the correction significantly reduces the dimension of the parent triple excitation subspace needed in the iterative part of the calculations. Simultaneously, it enables to reproduce the exact CCSDT results to an accuracy level below 0.1 kJ/mol with a larger, yet still reasonable, dimension of the parent excitation.
subspace. This typically can be achieved at a computational cost only several times larger than required for the CCSD(T) method. The proposed method retains black-box features of the single-reference coupled-cluster theory; the dimension of the parent excitation subspace remains the only additional parameter that has to be specified.
1 Introduction

Over the past decades coupled-cluster (CC) theory\textsuperscript{1–6} has been propelled into the position of one of the most important electronic structure methods. This success can be largely attributed to the rigorous size-extensivity as well as rapid convergence towards the full configuration-interaction limit with the excitation level, see Refs. 7,8 for recent reviews. However, these virtues come at a price of a rather steep scaling of the computational costs of the calculations with the system size. Therefore, many approaches such as optimized virtual orbital space,\textsuperscript{9–12} frozen natural orbitals,\textsuperscript{13–16} orbital-specific virtuals,\textsuperscript{17–20} and local correlation treatments based on local pair natural orbitals\textsuperscript{21–25} were proposed in the literature to alleviate this problem. Recently, a new idea to reduce the cost of CC (and related) methods has emerged which draws inspiration from the field of applied mathematics\textsuperscript{26} and employs tensor decomposition techniques to the wavefunction parameters.\textsuperscript{27–38} These techniques rely on representing the information contained in the cluster excitation amplitudes by a combination of lower-rank quantities. While the basic idea is simple enough, the real difficulty lies in selecting a suitable excitation subspace and then solving the CC equations within this subspace without “unpacking” the compressed quantities to their initial rank at any stage of the calculations. In parallel, similar ideas have also been applied to compression of electron repulsion integrals (ERI) leading to the development of the tensor hypercontraction (THC) format\textsuperscript{39,40} and its efficient implementations\textsuperscript{41–45} which enabled to reduce the scaling of various electronic structure methods.\textsuperscript{46–55}

Recently we have reported\textsuperscript{38} application of the Tucker-3 decomposition\textsuperscript{56,57} to the full CCSDT theory\textsuperscript{58,59} with the CC triply-excited amplitudes tensor represented as (details of the notation are given further in the text)

\[ t_{ijk}^{abc} \approx t_{XYZ} U_{ai}^{X} U_{bj}^{Y} U_{ck}^{Z}. \]  \hspace{1cm} (1)

The expansion tensors $U_{ai}^{X}$ are obtained upfront by higher-order singular-value decomposi-
tion (SVD) of approximate amplitudes, and the quantity \( t_{XYZ} \) is the compressed amplitude tensor. The method based on Eq. (1) shall be referred to as SVD-CCSDT in the remainder of the text. The main advantage of the decomposition format (1) is that the effective dimension of the \( t_{XYZ} \) tensor that is sufficient to maintain a constant relative accuracy in the correlation energy grows only linearly with the system size, \( N \). Without the compression, i.e., if all possible excitations were included in Eq. (1), this dimension would grow quadratically. This reduction solves two important problems associated with the application of the CCSDT theory to larger systems. First, the memory storage requirements are reduced from being proportional to \( N^6 \) to the level of \( N^4 \) because the full-rank amplitudes \( t^{abc}_{ijk} \) are never explicitly formed and only their compressed counterparts (\( t_{XYZ} \)) are stored. Second, by careful factorization of the CC equations and manipulating the order of tensor contractions one can reduce the scaling of the computational costs from \( N^8 \) (characterizing for the uncompressed CCSDT method) down to \( N^6 \).

In this work we expand upon the rank-reduced CCSDT theory introduced in Ref. 38. We propose a non-iterative, i.e., single-step, energy correction added on top of the SVD-CCSDT result. The purpose of this correction is to reduce the error with respect to the exact (uncompressed) CCSDT method by approximately accounting for triple excitations absent in the parent SVD subspace. The idea of adding a non-iterative correction to a converged coupled cluster result in order to account for, e.g., higher excitations excluded from the iterative model, is not new. In fact, numerous approaches have been proposed in the literature to derive such corrections. Historically, the first developments of this type were guided by the ordinary Møller-Plesset perturbation theory\(^{60}\) where the Hartree-Fock determinant serves as the zeroth-order wavefunction. However, this approach turned out to be suboptimal as best exemplified by the success of the CCSD(T) theory\(^{61}\) over the earlier CCSD[T] method.\(^{62}\) The latter is based solely on the usual perturbative arguments while the former includes, seemingly arbitrarily, a single higher-order term (out of many possible). A justification of this choice was presented by Stanton\(^{63}\) who treated CCSD as the zeroth-
order state and employed a formalism rooted in the equation-of-motion (EOM) theory\textsuperscript{64} to derive the non-iterative correction. With the help of Löwdin’s partitioning technique of the EOM Hamiltonian one can then show that the troubling higher-order term appears naturally and should be treated on an equal footing. The EOM-like formalism was further developed and refined by Gwaltney and Head-Gordon\textsuperscript{65,66} who derived a complete second-order correction to the CCSD energy, termed CCSD(2). Subsequent work in this field by Hirata and collaborators\textsuperscript{67–69} culminated in the introduction of the CC(m)PT(n) systematic hierarchy of methods. Sometime later the lack of order-by-order size consistency of the EOM-like approaches was recognized.\textsuperscript{70} Eriksen \textit{et al.}\textsuperscript{71} showed how this problem can be avoided if non-iterative corrections are derived by expanding the CC Langrangian of a higher-order method around a lower-order one. This leads to a hierarchy of methods such as CCSD(T-n) and CCSDT(Q-n) which are rigorously size-extensive in each order \( n \) separately, not only in their limit. A similar Lagrangian-based formulation was constructed by Kristiansen \textit{et al.}\textsuperscript{72} and showed an improved convergence characteristics. The size-consistency problems are also avoided in the framework of cluster perturbation theory developed by Pawłowski and collaborators.\textsuperscript{73–77} It is also important to point out the papers of Piecuch and collaborators\textsuperscript{78–81} who derived non-iterative corrections to the CC methods employing the so-called method-of-moments CC theory. This methodology has been progressively refined over the years, with recent introduction of an impressively general CC\((P;Q)\) hierarchy.\textsuperscript{82–84}

While the body of work published in the literature that deals with derivation of non-iterative corrections to the CC energies is large, none of the available formulas can be applied straight away in the SVD-CCSDT context without encountering serious problems of either theoretical or practical nature. These difficulties stem from the fact that in the SVD-CCSDT theory the parent triples excitation subspace is not spanned by some set of individual excitations. Instead, the basis of this subspace is composed of linear combinations of triple excitations which are found automatically by a procedure described in Ref. 37. To accommodate this problem we introduce a partitioning of the triple excitation space and generalize the
Langrangian formalism of Eriksen et al.\textsuperscript{70} This leads to a formula for a non-iterative energy correction that is similar in nature to the celebrated CCSD(T) method and, critically, can also be evaluated with the computational cost proportional to $N^7$.

The practical reason for introducing the non-iterative correction is twofold. First, it has been shown in Ref. 38 that the practical accuracy limit of the SVD-CCSDT method is, on average, a fraction of kJ/mol in relative energies. Provided that this level of accuracy is sufficient for the task at hand, the non-iterative correction enables a considerable reduction of the dimension of the parent excitation subspace needed in the iterative part of the calculations. This is advantageous because for small parent subspaces the timing of the SVD-CCSDT calculations is only a small multiple of the CCSD calculations for the same system. Simultaneously, we show that the inclusion of the non-iterative correction allows to reduce the error with respect to the uncompressed CCSDT by roughly an order of magnitude. Therefore, if the SVD subspace is large enough, accuracy levels below 0.1 kJ/mol become accessible. One can expect this accuracy to be sufficient in all but the most accurate studies concerning polyatomic molecules. In fact, other sources of error, such basis set incompleteness, are typically of the same magnitude or larger.

2 Theory

2.1 Preliminaries

For the convenience of the readers we begin by defining the notation that is adopted throughout the present paper and provide a short outline of the SVD-CCSDT theory. We employ the canonical Hartree-Fock (HF) determinant, denoted $|\phi_0\rangle$, as the reference wavefunction. The orbitals that are occupied in the reference are denoted by the symbols $i, j, k$, etc., and the unoccupied (virtual) orbitals by the symbols $a, b, c$, etc. When the occupation of the orbital is not specified general indices $p, q, r$, etc. are employed. The number of occupied and virtual orbitals in a given system is written as $O$ and $V$, respectively. The HF orbital
energies are denoted by $\epsilon_p$. For further use we also introduce the following conventions: $\langle A \rangle \overset{\text{def}}{=} \langle \phi_0 | A | \phi_0 \rangle$ and $\langle A | B \rangle \overset{\text{def}}{=} \langle A \phi_0 | B \phi_0 \rangle$ for arbitrary operators $A$, $B$. The Einstein convention for summation over repeated indices is employed unless explicitly stated otherwise. The standard partitioning of the electronic Hamiltonian, $H = F + W$, into the sum of the Fock operator ($F$) and the fluctuation potential ($W$) is adopted throughout the paper.

The SVD-CCSDT method is a variant of the CC theory and employs the exponential parametrization of the electronic wavefunction, $|\Psi\rangle = e^{T_{\text{SVD}}} |\phi_0\rangle$. The cluster operator $T_{\text{SVD}}$ contains single, double, and triple excitation operators, $T_{\text{SVD}} = T_1 + T_2 + T_{3\text{SVD}}$. The singly and doubly excited components assume the same form as in the uncompressed CCSDT theory

$$T_1 = t^a_i E_{ai}, \quad T_2 = \frac{1}{2} t^{ab}_{ij} E_{ai} E_{bj}, \quad (2)$$

where $t^a_i$, $t^{ab}_{ij}$ are the cluster amplitudes, and $E_{pq} = p^\dagger_\alpha q_\alpha + p^\dagger_\beta q_\beta$ are the spin-adapted singlet orbital replacement operators. The triply excited amplitudes $t_{ijk}^{abc}$ are subject to the Tucker-3 compression, see Eq. (1), and hence the triple excitation operator reads

$$T_{3\text{SVD}}^{\text{SVD}} = \frac{1}{6} t^{abc}_{ijk} E_{ai} E_{bj} E_{ck} = \frac{1}{6} t_{XYZ} U^X U^Y U^Z, \quad (3)$$

where $U^X = U^X_{ai} E_{ai}$. Throughout this paper the symbols $X$, $Y$, $Z$ are employed to denote the elements of the parent subspace (SVD subspace) of the triply excited amplitudes. The length of the expansion in Eq. (1) is denoted by $N_{\text{SVD}}$. For further use we also define the symbols $|a_i\rangle = E_{ai} |\phi_0\rangle$, $|ab_{ij}\rangle = E_{ai} E_{bj} |\phi_0\rangle$, etc., to denote excited-state configurations and similarly

$$|XYZ\rangle = U^X_{ai} U^Y_{bj} U^Z_{ck} |abc_{ijk}\rangle = U^X U^Y U^Z |\phi_0\rangle. \quad (4)$$

The amplitudes $t^a_i$, $t^{ab}_{ij}$, and $t_{XYZ}$ are found by solving the SVD-CCSDT equations obtained
by projecting $e^{-T_{\text{SVD}}} H e^{T_{\text{SVD}}} |\phi_0\rangle = 0$ onto the proper subset of excited configurations. The expansion vectors $U^{X}_{ai}$ are obtained upfront by singular-value decomposition of an approximate triples amplitude tensor

$$^2 \langle ijk | (\epsilon_{ij} - 1) \langle ij | [\tilde{W}, T_2] \rangle \rangle, \quad (5)$$

rewritten as a $OV \times O^2V^2$ rectangular matrix. The symbol $\epsilon_{ijk} = \epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c$ stands for the three-particle energy denominator and $\tilde{W} = e^{-T_1} W e^{T_1}$ is the $T_1$-transformed fluctuation potential. To obtain the optimal compression of the full tensor $t_{ijk}^{abc}$ to a desired size ($N_{\text{SVD}}$) one has to retain only those vectors $U^{X}_{ai}$ that correspond to the largest singular values.

In the previous papers devoted to the rank-reduced CC methods including triple excitations, the SVD of Eq. (5) was computed using an iterative bidiagonalization method. While this method is completely general, it scales as $N^7$ with the system size, more steeply than $N^6$ cost of the SVD-CCSDT iterations. While it has been shown\(^{38}\) that the prefactor of the former procedure is small and finding the SVD subspace does not constitute a bottleneck at present, this may change for larger molecules. To avoid this problem in this work we propose an alternative algorithm for determination of the parent triple excitations subspace from the approximate amplitudes (5). A detailed derivation of the method is included in the Supporting Information, along with numerical examples that confirm its reliability. The new algorithm gives exactly same results as its predecessor (assuming exact arithmetic), but it possesses a rigorous $N^6$ scaling of the computational costs with the system size which is advantageous in applications to larger systems. Moreover, the new method is non-iterative in nature which eliminates possible accumulation of numerical noise and convergence problems one may encounter in iterative schemes. The proposed method is used by default in all SVD-CCSDT calculations reported further in the paper.

To decompose the four-index electron repulsion integrals tensor, $(pq|rs)$, we employ the
robust density-fitting approximation\textsuperscript{86–90} (in the Coulomb metric)

\( (pq|rs) \approx B_{pq}^Q B_{rs}^Q, \quad \text{with} \quad B_{pq}^Q = (pq|P) [V^{-1/2}]_{PQ}, \tag{6} \)

where \( (pq|P) \) and \( V_{PQ} = (P|Q) \) are the three-center and two-center electron repulsion integrals, respectively, as defined in Ref. 91. The capital letters \( P, Q \) are employed throughout the present work to denote the elements of the auxiliary basis set (ABS). The formula (6) preserves all physical symmetries and positive-definiteness of the initial electron repulsion integrals tensor.\textsuperscript{92} The number of ABS functions is denoted \( N_{\text{aux}} \) further in the text and it scales linearly with the size of the system. The same formula is applied also for the \( T_1 \)-transformed two-electron integrals,\textsuperscript{93} \( (pq|rs) \approx B_{pq}^Q B_{rs}^Q \), that correspond to the similarity-transformed Hamiltonian \( \tilde{H} = e^{-T_1} H e^{T_1} \). The only difference is that the three-center integrals \( B_{pq}^Q \) are given in the \( T_1 \)-transformed, rather than the canonical, orbital basis. Let us also point out that all equations derived in the present work remain valid also for the Cholesky decomposition\textsuperscript{94–97} of the electron repulsion integrals since both methods share the same formal expression, Eq. (6).

### 2.2 Partitioning of the triple excitation subspace

The complete space of triple excitations is defined as \( \text{span}(\mu_3) \), where the symbol \( \text{span}(S) \) stands for a linear span of a set of vectors \( S \), and \( \mu_3 \) is the following set

\[ \mu_3 = \left\{ |abc\rangle \mid a < b \leq c \right\}. \tag{7} \]

Note that the set of vectors \( \mu_3 \) is not linearly independent; for example, among six possible functions \( |abc\rangle \), \( a < b < c \), with a fixed set of indices only five are independent\textsuperscript{85} as a
consequence of the relation

$$|abc⟩_{ijk} + |abc⟩_{ikj} + |abc⟩_{kji} + |abc⟩_{kij} + |abc⟩_{jki} = 0.$$  (8)

However, we require only that $\mu_3$ spans the complete space of triple excitations and the fact that it is not minimal bears no negative consequences in the present context. Next we introduce a set composed of the SVD vectors

$$\mu_3^{\text{SVD}} = \left\{ |XYZ⟩ \mid X \leq Y \leq Z \right\},$$  (9)

where $|XYZ⟩$ was defined in Eq. (4). The span of this set, $\text{span}(\mu_3^{\text{SVD}})$, is shortly referred to as the parent subspace or the SVD subspace. In general, the set $\mu_3^{\text{SVD}}$ may also contain linearly dependent elements. Finally, the third set of vectors, $\mu_3^{\perp}$, spans the orthogonal complement of $\mu_3^{\text{SVD}}$. This means that $\mu_3^{\perp}$ has the following two properties

$$\text{span}(\mu_3^{\text{SVD}} \cup \mu_3^{\perp}) = \text{span}(\mu_3),$$  (10)
$$\langle \mu_3^{\text{SVD}} | \mu_3^{\perp} \rangle = 0,$$  (11)

where the second equation is understood to hold separately for each pair of vectors from the sets $\mu_3^{\text{SVD}}$ and $\mu_3^{\perp}$. A natural way to generate the vectors $\mu_3^{\perp}$ is to project out the set $\mu_3^{\text{SVD}}$ from $\mu_3$. This choice is not unique, but the final results of this work do not depend on a particular procedure employed to generate $\mu_3^{\perp}$ provided that the relationships (10) and (11) are strictly true.

To simplify the subsequent derivations we have to specify how the Fock operator acts within the SVD subspace and its orthogonal complement. First, it is convenient to exploit the rotational freedom among the quantities $U^X_{ai}$ and enforce the relationship $U^X_{ai} U^Y_{ai} (\epsilon_i - \epsilon_a) = \epsilon_X \delta_{XY}$, where $\epsilon_X$ are some real-valued constants. This makes the Fock operator diagonal in
the SVD subspace in the sense that

\[ \langle X'Y'Z'|F|XYZ \rangle = (\epsilon_X + \epsilon_Y + \epsilon_Z) \delta_{XX'} \delta_{YY'} \delta_{ZZ'}. \] (12)

In the present work we assume a stronger condition that the SVD subspace is closed under the action of the Fock operator. In other words

\[ F|XYZ \rangle = (\epsilon_X + \epsilon_Y + \epsilon_Z) |XYZ \rangle, \] (13)

which, in general, constitutes an approximation when the SVD subspace is not complete. An immediate consequence of Eq. (13) is the relationship

\[ \langle \mu_3^{\text{SVD}}|F|\mu_3^\perp \rangle = \langle \mu_3^\perp|F|\mu_3^{\text{SVD}} \rangle = 0, \] (14)

which plays an important role in the derivations presented in the next section. The accuracy of this approximation depends on the size of the SVD subspace and in Sec. 3 we present a numerical verification of Eq. (14) for realistic systems.

For consistency, we additionally introduce sets \( \mu_1 = \{ |i \rangle \} \) and \( \mu_2 = \{ |ab \rangle | a \leq b \} \), so that \( \text{span}(\mu_1) \) and \( \text{span}(\mu_2) \) are complete spaces of single and double excitations, respectively.

### 2.3 Perturbative correction to the SVD-CCSDT energy

In this subsection we derive a non-iterative correction that approximately accounts for triple excitations excluded from the parent SVD subspace. First, we introduce the SVD-CCSDT Lagrangian\(^{98-103}\) and briefly discuss its most salient features. Next, we follow the idea of Eriksen et al.\(^ {70}\) and expand the Lagrangian of the exact CCSDT method around the SVD-CCSDT Lagrangian; the difference between them defines the desired energy correction. Finally, a perturbative scheme is introduced which allows to extract the components of the energy correction that are of the leading order in the fluctuation potential.
Let us begin by defining the Lagrangian\textsuperscript{98–103} of the SVD-CCSDT method. To this end we introduce the second excitation operator $\mathcal{L}_{\text{SVD}} = 1 + \mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_{3}^{\text{SVD}}$ which is fully analogous to the usual cluster operator $T_{\text{SVD}}$ defined by Eqs. (2) and (3), but contains the additional unity term*. For simplicity, the triply excited component $\mathcal{L}_{3}^{\text{SVD}}$ is expanded in the same SVD subspace as $T_{3}^{\text{SVD}}$. For brevity, further in the text we refer to the amplitudes of $\mathcal{L}_{\text{SVD}}$ as “multipliers”.

Under these provisions we can write down the SVD-CCSDT Lagrangian in full form

$$L_{\text{SVD}} = \langle \mathcal{L}_{\text{SVD}} | e^{-T_{\text{SVD}}} H e^{T_{\text{SVD}}} \rangle. \quad (15)$$

By recalling the SVD-CCSDT amplitude equations\textsuperscript{38}

$$\langle \mu_n | e^{-T_{\text{SVD}}} H e^{T_{\text{SVD}}} \rangle = 0, \quad n = 1, 2, \quad (16)$$

$$\langle \mu_3^{\text{SVD}} | e^{-T_{\text{SVD}}} H e^{T_{\text{SVD}}} \rangle = 0, \quad (17)$$

one can show the value of $L_{\text{SVD}}$ is equal to the SVD-CCSDT correlation energy for converged $T_{\text{SVD}}$ amplitudes. Additionally, by construction $L_{\text{SVD}}$ is variational with respect to the $\mathcal{L}_{\text{SVD}}$ amplitudes. However, in contrast to the usual CC energy formula, we require that this quantity is variational also with respect to the cluster amplitudes $T_{\text{SVD}}$. Minimization over $T_{\text{SVD}}$ gives the following set of linear equations for the multipliers

$$\langle \mathcal{L}_{\text{SVD}} | \left[ \overline{H}, \mu_n \right] \rangle = 0, \quad n = 1, 2, \quad (18)$$

$$\langle \mathcal{L}_{\text{SVD}} | \left[ \overline{H}, \mu_3^{\text{SVD}} \right] \rangle = 0, \quad (19)$$

where we have introduced a shorthand notation $\overline{H} = e^{-T_{\text{SVD}}} H e^{T_{\text{SVD}}}$ for the similarity-transformed SVD-CCSDT Hamiltonian. Completely analogous definitions of the Lagrangian

\*Note that the operator $\mathcal{L}_{\text{SVD}}$ is usually written in the literature\textsuperscript{8} as $\mathcal{L}_{\text{SVD}} = 1 + \Lambda$, where $\Lambda$ is a pure de-excitation operator, but this notation is not particularly convenient from the point of view of the present work.
hold for the exact (uncompressed) CCSDT theory. By denoting the exact CCSDT amplitudes by \(T\) and the auxiliary operator by \(\mathcal{L}\), the CCSDT Lagrangian is written as \(L_T = \langle \mathcal{L} | e^{-T} He^T \rangle\). The equations defining \(\mathcal{L}\) are again found by requiring that the Lagrangian is variational with respect to the cluster amplitudes.

Our first goal is to parametrize the exact CCSDT Lagrangian \((L_T)\) around the SVD-CCSDT Lagrangian \((L_{SVD})\) following the idea of Eriksen et al.\(^{70}\) To this end we rewrite the CCSDT cluster operators as \(T = T_{SVD} + \delta T\) and \(\mathcal{L} = \mathcal{L}_{SVD} + \delta \mathcal{L}\), where \(\delta T\) and \(\delta \mathcal{L}\) are the correction terms that have to be determined. They can be further expanded as

\[
\delta T = \delta T_1 + \delta T_2 + \delta T_{3 \text{SVD}} + \delta T_{3 \perp},
\]

and analogously for the second quantity \(\delta \mathcal{L}\). As the notation suggests, the components \(\delta T_{3 \text{SVD}}\) and \(\delta T_{3 \perp}\) include excitations only to the configurations belonging to \(\mu_{3 \text{SVD}}\) and \(\mu_{3 \perp}\), respectively. Because the two subspaces are orthogonal there is no double-counting of the excitations; moreover, the sum of both operators covers all possible excitations in the system. The division introduced in Eq. \((20)\) also has a clear interpretation – the operators \(\delta T_1\), \(\delta T_2\), and \(\delta T_{3 \text{SVD}}\) are responsible for “relaxation” of the excitation amplitudes that are already included in the SVD-CCSDT wavefunction, while the operator \(T_{3 \perp}\) corrects for the excitations outside the SVD subspace.

Let us to rewrite the exact CCSDT Lagrangian as

\[
L_T = \langle \mathcal{L}_{SVD} + \delta \mathcal{L} | e^{-\delta T} He^{\delta T} \rangle,
\]

and employ the nested commutator expansion to eliminate the operator exponentials. After
some rearrangements one obtains

\[ L_T = \langle \mathcal{L}_{\text{SVD}} | \overline{H} \rangle + \langle \delta \mathcal{L} | \overline{H} \rangle + \langle \mathcal{L}_{\text{SVD}} | [\overline{H}, \delta T] \rangle \]
\[ + \sum_{n=2}^{\infty} \frac{1}{n!} \langle \mathcal{L}_{\text{SVD}} | [\overline{H}, \delta T]_n \rangle + \sum_{n=1}^{\infty} \frac{1}{n!} \langle \delta \mathcal{L} | [\overline{H}, \delta T]_n \rangle \]

where \([X, Y]_n\) is a shorthand notation for \(n\)-tuply nested commutators, i.e. \([X, Y]_1 = [X, Y]\) and \([X, Y]_n = [[X, Y]_{n-1}, Y]\) for \(n \geq 2\). We immediately recognize the first term as the SVD-CCSDT Lagrangian, \(L_{\text{SVD}} = \langle \mathcal{L}_{\text{SVD}} | \overline{H} \rangle\), cf. Eq. (15). Therefore, further in the text we consider only the difference \(\delta E = L_T - L_{\text{SVD}}\) which is the desired energy correction. Next, we observe that \(\langle \delta \mathcal{L} | \overline{H} \rangle = \langle \delta \mathcal{L}_3^\perp | \overline{H} \rangle\), because projections on the other components of \(\mathcal{L}\), such as \(\langle \mathcal{L}_2 | \overline{H} \rangle\), vanish due to the SVD-CCSDT stationarity conditions, Eqs. (16) and (17). Next, the third term in the above equation can be rewritten as \(\langle \mathcal{L}_{\text{SVD}} | [\overline{H}, \delta T] \rangle = \langle \mathcal{L}_{\text{SVD}} | [\overline{H}, \delta T_3^\perp] \rangle\), because the remaining contributions are zero by the virtue of Eqs. (18) and (19). The last two terms in Eq. (22) remain unaltered at this point. We have arrived at the following formula for the energy correction

\[ \delta E = \langle \delta \mathcal{L}_3^\perp | \overline{H} \rangle + \langle \mathcal{L}_{\text{SVD}} | [\overline{H}, \delta T_3^\perp] \rangle + \sum_{n=2}^{\infty} \frac{1}{n!} \langle \mathcal{L}_{\text{SVD}} | [\overline{H}, \delta T]_n \rangle + \sum_{n=1}^{\infty} \frac{1}{n!} \langle \delta \mathcal{L} | [\overline{H}, \delta T]_n \rangle. \]

(23)

To proceed further we split the similarity-transformed Hamiltonian into two contributions, \(\overline{H} = \mathcal{F} + \mathcal{W}\), where \(\mathcal{F} = e^{-T_{\text{SVD}}} F e^{T_{\text{SVD}}}\) and \(\mathcal{W} = e^{-T_{\text{SVD}}} W e^{T_{\text{SVD}}}\). Note that since \(F\) is a one-electron operator we have \(F = F + [F, T_{\text{SVD}}]\), i.e. the multiply nested commutators vanish. Moreover, for any purely excitation operator \(X\) the relationship \([\mathcal{F}, X] = [F, X]\) holds. This allows to rewrite Eq. (23) as

\[ \delta E = \langle \delta \mathcal{L}_3^\perp | \mathcal{F} \rangle + \langle \delta \mathcal{L}_3^\perp | \mathcal{W} \rangle + \langle \mathcal{L}_{\text{SVD}} | [F, \delta T_3^\perp] \rangle + \langle \mathcal{L}_{\text{SVD}} | [W, \delta T_3^\perp] \rangle 
\[ + \langle \delta \mathcal{L} | [F, \delta T] \rangle + \sum_{n=2}^{\infty} \frac{1}{n!} \langle \mathcal{L}_{\text{SVD}} | [W, \delta T]_n \rangle + \sum_{n=1}^{\infty} \frac{1}{n!} \langle \delta \mathcal{L} | [W, \delta T]_n \rangle. \]

(24)
where all other terms involving $F$ vanished due to an inadequate excitation level. Up to this point we have introduced no approximations into this formalism. However, to simplify the equations further we invoke the condition (14) and set $\langle \mu_3^{\text{SVD}} | F | \mu_3^\perp \rangle = \langle \mu_3^\perp | F | \mu_3^{\text{SVD}} \rangle = 0$ whenever applicable. As discussed in Sec. 2.2 this is an approximation unless the SVD subspace is complete. By employing Eq. (14) one eliminates the first term of the above formula, because $\langle \delta L_3^\perp | F \rangle = \langle \delta L_3^\perp | [F, T_{\text{SVD}}] \rangle$, and the third term for the same reason. Therefore, we are left with

$$
\delta E = \langle \delta L | [F, \delta T] \rangle + \langle \delta L_3^\perp | W \rangle + \langle \mathcal{L}_{\text{SVD}} | [W, \delta T_3^\perp] \rangle 
+ \sum_{n=2}^{1} \frac{1}{n!} \langle \mathcal{L}_{\text{SVD}} | [W, \delta T]_n \rangle + \sum_{n=1}^{1} \frac{1}{n!} \langle \delta L | [W, \delta T]_n \rangle.
$$

(25)

By construction, the quantity given by Eq. (25) is variational both with respect to the cluster amplitudes and the multipliers. Therefore, a suitable set of equations for the perturbed amplitudes in $\delta L$ and $\delta T$ can be obtained by minimization. By differentiating Eq. (25) over the perturbed multipliers ($\delta L$) and equating the result to zero one obtains formulas for all components of the perturbed cluster amplitudes

$$
\langle \mu_m | [F, \delta T_m] \rangle + \sum_{n=1}^{1} \frac{1}{n!} \langle \mu_m | [W, \delta T]_n \rangle = 0, \quad m = 1, 2,
$$

(26a)

$$
\langle \mu_3^{\text{SVD}} | [F, \delta T_3^{\text{SVD}}] \rangle + \sum_{n=1}^{1} \frac{1}{n!} \langle \mu_3^{\text{SVD}} | [W, \delta T]_n \rangle = 0,
$$

(26b)

$$
\langle \mu_3^\perp | [F, \delta T_3^\perp] \rangle + \langle \mu_3^\perp | W \rangle + \sum_{n=1}^{1} \frac{1}{n!} \langle \mu_3^\perp | [W, \delta T]_n \rangle = 0,
$$

(26c)

Similarly, by minimization with respect to the cluster amplitudes ($\delta T$) one determines the
The formalism given above is not yet practically useful due to the computational cost being roughly the same as of the exact CCSDT theory. To eliminate this problem we set up a perturbative expansion of the above equations, treating the similarity-transformed Fock operator $\bar{F}$ as the zeroth-order quantity and the similarity-transformed fluctuation potential $\bar{W}$ as the first-order quantity. This leads to the expansion of the cluster amplitudes and the multipliers in the orders of the fluctuation potential $\delta T = \delta T(0) + \delta T(1) + \delta T(2) + \ldots$ (28) \[ \delta L = \delta L(0) + \delta L(1) + \delta L(2) + \ldots \] (29) where the order of a given term is indicated in the parentheses, e.g. $\delta T(n)$ is the $n$-th order component of $\delta T$. Similarly, the energy correction $\delta E$ is also rewritten as a sum $\delta E = \delta E(0) + \delta E(1) + \delta E(2) + \ldots$ At each perturbation order the cluster operators and multipliers are further split into the components corresponding different excitation manifolds, for example, $\delta T(n) = \delta T_1(n) + \delta T_2(n) + \delta T_3^{\text{SVD}}(n) + \delta T_3^\perp(n)$. The order-by-order expansions of the cluster amplitudes and multipliers are found by inserting Eqs. (28)–(29) into Eqs. (26a)–(27c). Subsequently, all terms of the same total order are grouped together and equated to zero. In this way one immediately finds that there are no zeroth-order contributions to the cluster amplitudes and multipliers, i.e. $\delta T(0) = 0$ and $\delta L(0) = 0$. Moreover, by analyzing Eqs. (26a)–(26c) one concludes that the only
first-order contribution to the perturbed cluster amplitudes is $\delta T_{3}^{\perp}(1)$ obtained from

$$\langle \mu_{3}^{\perp} | \left[ F, \delta T_{3}^{\perp}(1) \right] \rangle + \langle \mu_{3}^{\perp} | W \rangle = 0.$$  \hspace{1cm} (30)

The remaining first-order components vanish, i.e. $\delta T_{1}(1) = \delta T_{2}(1) = \delta T_{3}^{\text{SVD}}(1) = 0$. This means that the “relaxation” of the amplitudes corresponding to excitations already included in the SVD-CCSDT theory is of secondary importance and does not enter in the first order in the fluctuation potential. Similar conclusions hold for the multipliers where the only first-order contribution is $\delta L_{3}^{\perp}(1)$ and reads

$$\langle \delta L_{3}^{\perp}(1) | \left[ F, \mu_{3}^{\perp} \right] \rangle + \langle L_{\text{SVD}} | \left[ W, \mu_{3}^{\perp} \right] \rangle = 0,$$  \hspace{1cm} (31)

and $\delta L_{1}(1) = \delta L_{2}(1) = \delta L_{3}^{\text{SVD}}(1) = 0$. In the second order we obtain the following expressions for the perturbed cluster amplitudes

$$\langle \mu_{m} \left| F, \delta T_{m}(2) \right\rangle + \langle \mu_{m} \left| W, \delta T_{3}^{\perp}(1) \right\rangle = 0, \quad m = 1, 2,$$  \hspace{1cm} (32a)

$$\langle \mu_{3}^{\text{SVD}} \left| F, \delta T_{3}^{\text{SVD}}(2) \right\rangle + \langle \mu_{3}^{\text{SVD}} \left| W, \delta T_{3}^{\perp}(1) \right\rangle = 0,$$  \hspace{1cm} (32b)

$$\langle \mu_{3}^{\perp} \left| F, \delta T_{3}^{\perp}(2) \right\rangle + \langle \mu_{3}^{\perp} \left| W, \delta T_{3}^{\perp}(1) \right\rangle = 0,$$  \hspace{1cm} (32c)

where we see, for the first time, a non-vanishing “relaxation” contribution. The second-order contributions to the multipliers are similarly found from the equations

$$\langle \delta L_{m}(2) \left| F, \mu_{m} \right\rangle + \langle \delta L_{3}^{\perp}(1) \left| W, \mu_{m} \right\rangle + \langle L_{\text{SVD}} \left| \left[ \left[ W, \delta T_{3}^{\perp}(1) \right], \mu_{m} \right] \right\rangle = 0, \quad m = 1, 2,$$  \hspace{1cm} (33)

and analogously for the $\delta L_{3}^{\text{SVD}}(2)$ component. The second-order contribution to $\delta L_{3}^{\perp}$ vanishes, i.e. $\delta L_{3}^{\perp}(2) = 0$, because the only relevant second-order term in Eq. (27c), namely $\langle L_{\text{SVD}} \left| \left[ \left[ \mu_{m} \left| \left[ W, \delta T_{3}^{\perp}(1) \right], \mu_{3}^{\perp} \right\rangle, \right\rangle \right\rangle$, is zero due to conflicting excitation levels in bra and ket.

The major practical advantage of the order-by-order expansion in comparison with the
initial formulation given by Eqs. (26a)–(27c) is the fact that at each level the highest-order contribution to $\delta L$ and $\delta T$ appears only in the commutator with the Fock operator, e.g. $\langle \mu_3^+ | [F, \delta T_3^+(n)] \rangle$ or $\langle \delta \mathcal{L}_3^+(n) | [F, \mu_3^+] \rangle$. This allows to invert each equation explicitly in a one step procedure, in contrast to Eqs. (26a)–(27c) which require an iterative procedure to solve.

Having determined the order-by-order expansion of $\delta T$ and $\delta L$ we proceed to the derivation of the corresponding energy corrections based on Eq. (25). Since there are no zeroth-order contributions in $\delta T$ and $\delta L$ one can easily show that $\delta E(0) = 0$. Moreover, an inspection of Eq. (25) proves that $\delta E(1)$ also vanishes and hence the energy corrections start at the second order in the fluctuation potential. To derive the higher-order corrections one has to keep in mind that the expression for $\delta E$ constructed above is variational with respect to $\delta T$ and $\delta L$. As a result, the corrections $\delta E(n)$ obey the so-called Wigner rules. These rules state that for a given $n$, $\delta T(n)$ is sufficient to calculate corrections up to $E(2n + 1)$, while $\delta L(n)$ – up to $\delta E(2n + 2)$. Guided by these rules we find the following expressions for $\delta E(n)$ up to the fourth order:

\[
\begin{align*}
\delta E(2) &= \langle \mathcal{L}_{\text{SVD}} | [\overline{W}, \delta T_3^+(1)] \rangle, \\
\delta E(3) &= \langle \mathcal{L}_3^+(1) | [\overline{W}, \delta T_3^+(1)] \rangle, \\
\delta E(4) &= \langle \mathcal{L}_3^+(1) | [\overline{W}, \delta T(2)] \rangle + \langle \mathcal{L}_{\text{SVD}} | [ [\overline{W}, \delta T_3^+(1)], \delta T_1(2) + \delta T_2(2) ] \rangle.
\end{align*}
\]

Note that the aforementioned “relaxation” of the cluster amplitudes, represented by $\delta T_1(2)$, $\delta T_2(2)$, and $\delta T_{3,\text{SVD}}(2)$ operators, contributes for the first time in surprisingly high orders. The components $\delta T_1(2)$ and $\delta T_2(2)$ appear for the first time in $\delta E(4)$, while $\delta T_{3,\text{SVD}}(2)$ does not enter until the fifth order.

In this work we concentrate on the leading-order correction to the SVD-CCSDT energy, $\delta E(2)$, given by Eq. (34a). In this paragraph we bring this equation to an explicit form, more suitable for further manipulations. First, note that Eq. (34a) can be equivalently
rewritten as

\[ \delta E(2) = \langle \mathcal{L}_{\text{SVD}}|\mathcal{H}, \delta T_{3}^{\perp}(1) \rangle, \quad (35) \]

because \( \mathcal{H} = \mathcal{F} + \mathcal{W} \), and \( \langle \mathcal{L}_{\text{SVD}}|\mathcal{F}, \delta T_{3}^{\perp}(1) \rangle = \langle \mathcal{L}_{\text{SVD}}|\mathcal{F}, \delta T_{3}^{\perp}(1) \rangle = 0 \). The latter equality is valid due to the condition (14) and conflicting excitation levels in bra and ket. Next, we observe that Eq. (30) which defines the operator \( \delta T_{3}^{\perp}(1) \) can be simplified to the form

\[ \langle \mu_{3}|F, \delta T_{3}(1) \rangle + \langle \mu_{3}|\mathcal{H} \rangle = 0. \quad (36) \]

To derive this equation we exploited the facts that \( \langle \mu_{3}^{\perp}|\mathcal{W} \rangle = \langle \mu_{3}^{\perp}|\mathcal{H} \rangle \) and \( \langle \mu_{3}^{\perp}|\mathcal{H} \rangle = \langle \mu_{3}|\mathcal{H} \rangle \). The former relationship is a direct consequence of Eq. (14) while the latter holds due to the SVD-CCSDT stationarity condition, i.e., \( \langle \mu_{3}^{\text{SVD}}|\mathcal{H} \rangle = 0 \). The advantage of Eq. (36) in comparison to Eq. (30) is that it can be explicitly solved since the Fock operator is diagonal in the basis of canonical molecular orbitals. By combining Eqs. (35) and (36) we arrive at

\[ \delta E(2) = -\left(\epsilon_{ij}^{abc}\right)^{-1} \langle \mathcal{L}_{1} + \mathcal{L}_{2} + \mathcal{L}_{3}^{\text{SVD}}|\mathcal{H}_{ij}^{abc}\rangle \langle \mathcal{H}_{ij}^{abc}|\mathcal{H} \rangle. \quad (37) \]

Note that the manipulations outlined above allowed to remove the complementary subspace \( \mu_{3}^{\perp} \) from the final working expression, eliminating the need to explicitly find the basis of \( \mu_{3}^{\perp} \). However, this may no longer be possible in higher orders.

The equation (37) constitutes the backbone of our formalism. However, for pragmatic reasons we introduce two additional approximations. They are not necessary to make the method practically feasible, but nonetheless they reduce the cost of the calculations considerably without sacrificing much accuracy. First, we replace the \( \mathcal{L} \) amplitudes by the corresponding \( T_{\text{SVD}} \) cluster amplitudes, i.e., we set \( \mathcal{L}_{n} = T_{n}, \ n = 1, 2, \) and \( \mathcal{L}_{3}^{\text{SVD}} = T_{3}^{\text{SVD}} \), as is the usual practice in deriving non-iterative corrections accounting for higher-order excitations. This approximation eliminates the need to compute the SVD-CCSDT Lagrangian multipli-
ers which is comparably expensive to the SVD-CCSDT calculation itself. Nonetheless, we note that the inclusion of the Langrangian amplitudes in other non-iterative methods, such as $\Lambda$-CCSD(T), has been studied. An implementation of a related formalism in the SVD-CCSDT context is an interesting topic for a future work.

The second approximation is the neglect of the $L_{3}^{\text{SVD}}$ component in Eq. (37). We found that this term is numerically negligible in most cases, especially for smaller SVD subspaces. At the same time the calculation of this term, while possible to accomplish with a $N^7$ scaling, is technically complicated and possesses a rather large prefactor. Further in the paper we demonstrate that the omission of this term results in a method that is already capable of reaching sufficient accuracy levels. After taking into account the aforementioned approximations we arrive at the final formula

$$
\delta E_{T+} = - \left( \epsilon_{ijk}^{abc} \right)^{-1} \langle T_1 + T_2 | H_{ij}^{abc} / _{ijk} | H \rangle.
$$

(38)

For the brevity, the method that adds the correction (38) on top of the converged SVD-CCSDT energy is called SVD-CCSDT+ further in the text.

It is important to discuss two extreme cases of the formula (38): the case when the SVD subspace is empty, $\mu_3^{\text{SVD}} = \emptyset$, and the case when it spans the whole space of triple excitations, $\text{span}(\mu_3) = \text{span}(\mu_3^{\text{SVD}})$. The former case trivially corresponds to the CCSD calculations where $T_3^{\text{SVD}} = 0$ and the expression for the correction simplifies to

$$
\delta E_{T+} = - \left( \epsilon_{ijk}^{abc} \right)^{-1} \langle T_1 + T_2 | \tilde{F} + \tilde{W}_{ij}^{abc} | H \rangle + \frac{1}{2} \left[ \left[ \tilde{F} + \tilde{W}, T_2 \right], T_2 \right],
$$

(39)

where $\tilde{F} = e^{-T_1} F e^{T_1}$. If we additionally dropped all terms that are of quadratic and higher order in the cluster amplitudes we would obtain the expression defining the CCSD(T) theory. This means that for an empty SVD subspace results obtained with the SVD-CCSDT+ method should be close to the CCSD(T) theory, assuming that we are dealing with well-behaved systems where the norm of the cluster amplitudes is significantly smaller than the
unity. In the second extreme case \( \mu_3 = \mu_3^{SVD} \) it is straightforward to show that the \( \delta E_{T+} \) correction is rigorously equal to zero. This is a consequence of the fact that the term \( \langle abc | \mathcal{H} | ijk \rangle \) in Eq. (38), defining the CCSDT stationary condition, vanishes for \( \mu_3 = \mu_3^{SVD} \). This property of the \( \delta E_{T+} \) correction shows that the formula (38) does not introduce any spurious double-counting of excitations which would degrade the accuracy. However, note that if the term \( \langle abc | \mathcal{H} | ijk \rangle \) in Eq. (38) was approximated in any way, the zero limit of the correction would no longer be strictly guaranteed.

Finally, we discuss the computational cost of evaluating Eq. (38) and some details of the implementation. Explicit expressions for the residual \( \langle abc | \mathcal{H} | ijk \rangle \) expressed through cluster amplitudes and molecular integrals were given in Ref. 58 and there is no point in repeating them here. Therefore, for illustrative purposes we concentrate only on a single term in \( \langle abc | \mathcal{H} | ijk \rangle \) that determines the overall scaling of the method. It reads

\[
(1 + P_{bj,ck}) (1 + P_{ai,bj} + P_{ai,ck}) \left[ \chi_{ce}^{bd} t_{ijk}^{adec} \right],
\]  

(40)

where \( \chi_{ce}^{bd} \) is an intermediate quantity given by Eq. (13) in Ref. 38 and the symbol \( P_{ai,bj} \) denotes the permutation operator that exchanges pairs of indices \( i \leftrightarrow j \) and \( a \leftrightarrow b \) simultaneously. Without any simplifications the computational cost of this term scales as \( O^3 V^5 \propto N^8 \). However, by exploiting the decomposition format of the triply-excited amplitudes, Eq. (1), and properly arranging the order of tensor contractions the assembly of Eq. (40) can be decomposed into a series of steps

\[
(1 + P_{bj,ck}) (1 + P_{ai,bj} + P_{ai,ck}) \left[ U_{ai}^X \left[ \left( \chi_{ce}^{bd} U_{ek}^Z \right) U_{dj}^Y \right] t_{XYZ} \right],
\]  

(41)

where the parentheses indicate the sequence of operations. By recalling that \( N_{SVD} \) scales linearly with the system size one can show that each step scales as \( N^7 \) or less. The most expensive is the third step (counting from the innermost parentheses) scaling as \( O^2 N_{SVD}^3 V^2 \). In order to avoid memory bottlenecks the quantity \( \langle abc | \mathcal{H} | ijk \rangle \) is evaluated on-the-fly in batches.
with three fixed occupied indices \((ijk)\). Each batch is immediately consumed in evaluation of the respective contribution to \(\delta E_{T+}\), Eq. (38), and then discarded. This part of the algorithm is similar to the conventional scheme employed for evaluation of the \((T)\) correction (see, for example, Refs. 106–108) and possesses the same computational cost, namely \(O^3V^4 \propto N^7\). For small SVD subspace size, this cost is dominant in comparison with \(O^2N_{\text{SVD}}^3V^2\) necessary to assemble \(\langle abc \mid \mathcal{H} \rangle\). However, in more accurate calculations one expects that \(N_{\text{SVD}} \approx V\) and the computation of \(\langle abc \mid \mathcal{H} \rangle\) becomes the limiting step. In this regime it is also worthwhile to compare the cost of evaluating the SVD-CCSDT+ correction with a single SVD-CCSDT iteration. The latter is characterized by the \(OV^2N_{\text{SVD}}^3\) scaling, as discussed in Ref. 38, by a factor of \(O\) smaller than the computation of \(\langle abc \mid \mathcal{H} \rangle\). Therefore, the total cost of computing the \(\delta E_{T+}\) correction is predicted to be roughly comparable to \(O\) SVD-CCSDT iterations, assuming that the prefactors are of a similar magnitude and that \(N_{\text{SVD}} \approx V\). A detailed comparison of timings obtained for realistic systems is given further in the text. In Supporting Information we investigate the computational complexity of evaluating the \(\delta E_{T+}\) correction for a model system: linear alkanes with increasing chain length. Direct comparison of computational timings obtained reveals a slightly lower scaling (\(N^{6.37}\)) than predicted theoretically (\(N^7\)). This deviation is due to terms in the \(\delta E_{T+}\) correction that can be evaluated with \(N^5\) or \(N^6\) cost, but have a relatively large prefactor. Nonetheless, as the system size is increased further, the cost of such terms is going to decrease (on a relative basis), leading to the \(N^7\) scaling of the method.

3 Numerical results and discussion

3.1 Computational details

Unless explicitly stated otherwise, all calculations reported in this work employ the Dunning-type cc-pVTZ basis set.\(^{109}\) The corresponding density-fitting auxiliary basis set cc-pVTZ-MP2FIT was taken from the work of Weigend et al.\(^ {110,111}\) Pure spherical representation (5d,
Figure 1: Values of the $R$ coefficient, see Eq. (42), as a function of the SVD subspace size for the HF molecule (internuclear distance 0.917 Å, cc-pVTZ basis set). The black dashed lines are linear functions connecting two neighboring data points.

Density-fitting was employed by default at every stage of calculations apart from solving the Hartree-Fock equations where the exact two-electron integrals were used. Additionally, reference CCSDT results were obtained using the exact integrals because, to the best of our knowledge, no DF-CCSDT implementation is currently available. The uncompressed CCSDT calculations were performed with the help of the CFour program package. In all correlated calculations we employ the frozen-core approximation by dropping $1s^2$ core orbitals of the first-row atoms (Li–Ne).

### 3.2 Numerical verification of the condition (14)

The derivation of the SVD-CCSDT+ correction presented in Sec. 2.3 relies on the assumption that the SVD subspace is closed under the action of the Fock operator. When the SVD subspace is incomplete this constitutes an approximation whose quality has to be verified numerically. To quantify the accuracy of Eq. (13) we consider the action of the Fock operator
on the sum of all SVD vectors, i.e. \( \sum_{XYZ} F|XYZ\rangle \). For brevity, we introduce the symbol \( \Psi_{SVD} = \sum_{XYZ} |XYZ\rangle \). The function \( F\Psi_{SVD} \) is projected separately onto the SVD subspace and onto the full space of triple excitations. Finally, square norms of both projections are formed and the square root of their ratio is calculated. The resulting quantity measures the magnitude of the component of \( F\Psi_{SVD} \) that resides within the SVD subspace in relation to the total norm of the \( F\Psi_{SVD} \) function. Expressed mathematically, this reads

\[
R = \sqrt{\frac{\langle \Psi_{SVD}|F|XYZ\rangle \langle XYZ|F|\Psi_{SVD}\rangle}{\langle \Psi_{SVD}|F|abc\rangle \langle abc|F|\Psi_{SVD}\rangle}}.
\]

(42)

By construction, the coefficient \( R \) takes values between 0 and 1. In a situation when Eq. (14) is satisfied exactly one strictly has \( R = 1 \). Therefore, the deviation of the coefficient \( R \) from the unity is a quantitative measure of the accuracy of the condition (14). However, it is important to point out that is not guaranteed that the coefficient \( R \) vanishes monotonically as the SVD subspace size is increased.

As an illustrative example, we calculated the coefficient \( R \) as a function of the SVD subspace size for the hydrogen fluoride (HF) molecule (internuclear distance 0.917 Å). For this system the maximum size of the SVD subspace equals to 195. The results are presented in Fig. 1. The first important observation is that even for small SVD subspaces \( (N_{SVD} \approx 10) \) the values of the coefficient \( R \) are already larger than 0.95. This further increases above 0.98 when a larger number of SVD vectors are included \( (N_{SVD} \approx 50) \). Therefore, for SVD subspaces large enough to be practically useful, the error resulting from Eq. (13) should not exceed a few percent. Considering other possible sources of error, this is acceptable from the point of view of the present work. In Supporting Information we present additional numerical results analogous to Fig. 1 for other molecules. The conclusions of these calculations are essentially the same as discussed above.
3.3 Accuracy of the SVD-CCSDT+ method: total correlation energies

Before we present calculations of chemically-relevant quantities for larger molecular systems, it is advantageous to study errors of the SVD-CCSDT and SVD-CCSDT+ methods in reproduction of total correlation energies taking the exact CCSDT method as the reference. To this end we selected a set of 16 small molecules comprising 2 – 5 atoms. The list of the molecules together with their geometries in the Cartesian format are given in the Supporting Information. For each molecule we performed SVD-CCSDT and SVD-CCSDT+ calculations (cc-pVTZ basis set) with the size of the SVD subspace being linearly related to the total number of orbitals ($N_{MO}$) in a given system, that is $N_{SVD} = x \cdot N_{MO}$. We consider several representative values of the $x$ parameter, namely $x = \frac{1}{6}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{5}{6}, 1$. To minimize the impact of the density-fitting approximation on the computed correlation energies, we employ a large cc-pV5Z-RI auxiliary basis set. With this setup the results are virtually free of the density-fitting error which does not exceed a few parts per million in all cases.

Figure 2: Distribution of relative errors (in percent) in the SVD-CCSDT (left panel) and SVD-CCSDT+ (right panel) correlation energies with respect to the exact CCSDT method (cc-pVTZ basis set). The parameter $x$ defines the size of the triple excitation subspace, $N_{SVD} = x \cdot N_{MO}$, where $N_{MO}$ is the total number of orbitals in a given system. Notice the change of scale on the horizontal axis.
Further in this section we adopt the relative error in the correlation energy, defined as

$$\Delta_i = \frac{E_{\text{method},i} - E_{\text{CCSDT},i}}{E_{\text{CCSDT},i}},$$

as the size-intensive measure of the quality of the results. In Eq. (20) the index $i$ enumerates the molecules in the test set and the symbol “method” refers to either SVD-CCSDT or SVD-CCSDT+. To perform a statistical analysis of the results we calculated the mean relative error and its standard deviation

$$\bar{\Delta} = \frac{1}{n} \sum_{i=1}^{n} \Delta_i,$$

$$\Delta_{\text{std}}^2 = \frac{1}{n-1} \sum_{i=1}^{n} (\Delta_i - \bar{\Delta})^2,$$

where $n = 16$ is the number of molecules in the test set. We found that the statistical distribution of the relative error is approximately normal for each value of the $x$ parameter. Therefore, to simplify the presentation the quantities $\bar{\Delta}$ and $\Delta_{\text{std}}$ are represented graphically in Fig. 2 in terms of the Gaussian functions

$$\rho(\Delta) = N e^{-\left(\Delta - \bar{\Delta}\right)^2/2\Delta_{\text{std}}^2},$$

where $N$ is a constant chosen such that $\rho(\Delta)$ is normalized to the unity. Raw values of the quantities $\bar{\Delta}$ and $\Delta_{\text{std}}$ for all $x$ under consideration are given in the Supporting Information.

The results represented in Fig. 2 show that the SVD-CCSDT method has a tendency to underestimate the correlation energies for small $x$, but then it overshoots the exact results as $x$ is increased. For $x = 1$ the mean error of the SVD-CCSDT method is slightly above 0.1% and, as demonstrated in Ref. 38, further increase of the parameter $x$ leads to a smooth, albeit slower, convergence towards the exact value. The behavior of the SVD-CCSDT+ is both qualitatively and quantitatively different. First, the overshooting tendency is absent and the convergence is smooth starting with the smallest $x$ considered here. Second, the
magnitude of the error is reduced considerably; for example, for \( x = 1 \) the SVD-CCSDT+ method achieves the mean relative error of about \(-0.03\%\) which is by a factor of about four smaller than SVD-CCSDT. It is worth point out that for all molecules considered here, the SVD-CCSDT+ results approach their limit from above in a regular fashion. This opens up a possibility of extrapolation similar as in Refs. 115,116, but a detailed analysis of this problem is beyond the scope of the present work.

### 3.4 Accuracy of the SVD-CCSDT+ method: relative energies

In the previous we have considered the accuracy of the SVD-CCSDT+ method in reproduction of the total correlation energies. However, relative quantities are of prime importance in most practical situations. To analyze the accuracy and computational efficiency of the proposed method in the latter case we calculated isomerization energies for 20 organic systems from the set previously considered by Grimme et al.\(^{117}\) This set covers a wide range of
Table 1: Isomerization energies (in kJ/mol) for systems presented in Fig. 3 calculated with the SVD-CCSDT and SVD-CCSDT+ methods as a function of the SVD subspace size ($N_{\text{SVD}}$). For each reaction, the SVD-CCSDT results are given in the first row while the SVD-CCSDT+ results in the second row. The corresponding results obtained with the exact CCSDT method are given in the last column. The number of (active) occupied/virtual orbitals in each system is given in parentheses below the reaction numbers.

| no. | $N_{\text{SVD}}$ | 20  | 40  | 60  | 80  | 100 | 120 | 140 | 160 |
|-----|------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
| 2   |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
| 3   |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
| 4   |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
| 5   |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
| 6   |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |
|     |                  |     |     |     |     |     |     |     |     |

SVD-CCSDT iterations did not converge.

structural changes – from relatively simple cis-trans isomerizations to migrations of whole functional groups. Besides several reactions involving only hydrocarbons, we include examples that also involve heteroatoms (oxygen and nitrogen) to cover the most common
bonding situations found in organic molecules. The range of isomerization energies is also broad, spanning from only a few kJ/mol to hundreds of kJ/mol. The list of isomerization reactions is given in Fig. 3. They are arranged roughly in the order of increasing system size. The largest molecule considered in this work (reaction 20) contains 46 electrons (34 correlated) with 264 functions in the atomic basis set and 666 functions in the density-fitting basis set. All reactions given in Fig. 3 are formulated such that the isomerization energies are positive.

The isomerization reactions given in Fig. 3 are divided into two groups. The first group (reactions 1–9) involve relatively small molecular systems for which full (uncompressed) CCSDT computations are available. This allows to ascertain the accuracy of the SVD-CCSDT+ method unambiguously. The second group (reactions 11–20) includes also larger species for which the exact CCSDT calculations are not practical with our computational resources. For each isomerization reaction from Fig. 3 we carried out SVD-CCSDT calculations followed by evaluation of the SVD-CCSDT+ correction. The size of the SVD subspace was varied from $N_{\text{SVD}} = 20$ up to $N_{\text{SVD}} = 160$ in steps of 20. For the second group of reactions we additionally obtained results for $N_{\text{SVD}} = 180$ and $N_{\text{SVD}} = 200$ to fully converge the energy differences. The results for the first and second group of reactions are given in Tables 1 and 2, respectively.

We begin our analysis by considering the first group of reactions, see Table 1. Similarly as in the previous work, the SVD-CCSDT results converge rather quickly to the accuracy level of a fraction of 1 kJ/mol with increasing SVD subspace size. Beyond this point the convergence slows down (reactions 5 and 6) or even becomes mildly oscillatory (reactions 4 and 7). To reduce the error of the SVD-CCSDT method to the level of about 0.1 kJ/mol in all cases, a further increase of $N_{\text{SVD}}$ would be needed. This is similar to the accuracy of the SVD-CCSDT method for the total correlation energies reported in Sec. 3.3 and in Ref. 38, albeit for the isomerization energies we do not observe the overshooting tendency.

By adding the SVD-CCSDT+ correction the results improve considerably. The accuracy
of a fraction of 1 kJ/mol is achieved with significantly smaller SVD subspaces ($N_{\text{SVD}} = 40 - 60$). A further increase of $N_{\text{SVD}}$ to $\approx N_{\text{MO}}$ allows to stabilize the results to within 0.01–0.02 kJ/mol (or 0.02–0.03% on the relative basis) in most cases. Therefore, the overall behavior of the SVD-CCSDT+ method in calculation of the isomerization energies is similar as in the case of the total energies reported in Sec. 3.3. However, the improvement over the SVD-CCSDT is larger which suggests that the SVD-CCSDT+ method benefits from a more systematic error cancellation.

A puzzling feature of the SVD-CCSDT+ results is that despite the apparently tight convergence to within 0.01–0.02 kJ/mol for $N_{\text{SVD}} \approx N_{\text{MO}}$, the true errors with respect to the exact CCSDT are larger. On a relative basis, this phenomenon is most pronounced for reaction 2 where the SVD-CCSDT+ results for $N_{\text{SVD}} = 160$ are converged to within 0.01 kJ/mol, but the deviation from the exact CCSDT is about 0.09 kJ/mol. Some of this difference can clearly be attributed to the perturbative nature of the SVD-CCSDT+ method and additional simplifications described in Sec. 2.3. However, the density-fitting approximation of the two-electron integrals may also be suspected to bring a significant contribution to the observed deviation. In fact, density-fitting errors of a similar magnitude were observed in the DF-CCSD(T) method, see Ref. 16 for a detailed analysis. To study this issue we repeated the SVD-CCSDT+ calculations for reaction 2 within the same orbital basis set, but increased the size of the auxiliary basis set by one cardinal number. The isomerization energy obtained in this way for $N_{\text{SVD}} = 160$ turned out to be 4.47 kJ/mol, compared with 4.52 kJ/mol obtained previously. This reduced the deviation from the exact CCSDT result (4.43 kJ/mol) by a factor of two. Further increase of the size of the auxiliary basis leads to no appreciable improvement in the results. Therefore, we recommend to increase the size of the auxiliary basis set by one cardinal number in the SVD-CCSDT+ calculations if the accuracy of 0.1 kJ/mol or better is desired. Alternatively, other methods designed to reduce the density-fitting error can be adopted\textsuperscript{118,119} or the density-fitting approximation can be entirely replaced by the Cholesky decomposition\textsuperscript{94–97} where a stricter error control is
Table 2: Isomerization energies (in kJ/mol) for systems presented in Fig. 3 calculated with the SVD-CCSDT and SVD-CCSDT+ methods as a function of the SVD subspace size ($N_{\text{SVD}}$). For each reaction, the SVD-CCSDT results are given in the first row while the SVD-CCSDT+ results in the second row. The number of (active) occupied/virtual orbitals in each system is given in parentheses below the reaction numbers.

| no. | 20  | 40  | 60  | 80  | 100 | 120 | 140 | 160 | 180 | 200 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 10  | 133.22 | 133.27 | 132.53 | 132.18 | 131.54 | 131.46 | 131.23 | 131.27 | 131.02 |
| (12/188) | 130.80 | 130.65 | 130.75 | 130.65 | 130.63 | 130.54 | 130.53 | 130.54 | 130.53 |
| 11  | 4.97 | 5.06 | 4.63 | 4.78 | 4.67 | 4.71 | 4.79 | 4.67 | 4.73 | 4.68 |
| (12/216) | 4.57 | 4.69 | 4.66 | 4.61 | 4.65 | 4.63 | 4.64 | 4.64 | 4.65 | 4.65 |
| 12  | 3.90 | 4.45 | 4.90 | 4.19 | 4.66 | 4.67 | 4.57 | 4.63 | 4.59 | 4.55 |
| (12/216) | 4.59 | 4.66 | 4.66 | 4.67 | 4.66 | 4.64 | 4.66 | 4.65 | 4.65 | 4.65 |
| 13  | 118.61 | 117.90 | 117.66 | 117.68 | 117.63 | 117.08 | 116.95 | 116.61 | 116.45 | 116.46 |
| (13/215) | 116.44 | 116.28 | 116.25 | 116.20 | 116.17 | 116.10 | 116.11 | 116.10 | 116.10 | 116.09 |
| 14  | 273.71 | 270.06 | 271.01 | 270.74 | 269.29 | 268.74 | 268.46 | 268.27 | 268.13 | 268.08 |
| (13/187) | 268.00 | 267.62 | 267.62 | 267.45 | 267.42 | 267.37 | 267.34 | 267.32 | 267.31 | 267.30 |
| 15  | 77.34 | 76.29 | 76.00 | 76.46 | 75.56 | 76.76 | 75.52 | 75.70 | 75.53 | 75.55 |
| (15/215) | 75.66 | 75.57 | 75.59 | 75.55 | 75.57 | 75.51 | 75.50 | 75.50 | 75.48 | 75.48 |
| 16  | 19.89 | 18.37 | 20.51 | 19.74 | 20.88 | 19.94 | 20.15 | 19.81 | 20.02 | 19.87 |
| (15/215) | 18.99 | 19.37 | 19.41 | 19.49 | 19.44 | 19.47 | 19.46 | 19.45 | 19.46 | 19.46 |
| 17  | 49.24 | 49.70 | 50.08 | 49.95 | 50.63 | 50.82 | 51.91 | 52.49 | 52.56 | 52.71 |
| (15/242) | 52.70 | 52.84 | 52.90 | 52.98 | 53.02 | 53.03 | 53.01 | 53.02 | 53.02 | 53.02 |
| 18  | 27.75 | 24.90 | 25.20 | 25.54 | 25.60 | 25.72 | 25.88 | 26.08 | 26.10 | 26.22 |
| (14/243) | 26.98 | 26.79 | 26.78 | 26.85 | 26.82 | 26.80 | 26.82 | 26.82 | 26.83 | 26.83 |
| 19  | 39.52 | 40.35 | 40.14 | 39.54 | 39.69 | 39.48 | 39.59 | 39.24 | 39.02 | 39.01 |
| (15/228) | 38.60 | 38.70 | 38.61 | 38.63 | 38.60 | 38.59 | 38.57 | 38.54 | 38.53 | 38.53 |
| 20  | 58.98 | 59.41 | 59.21 | 59.03 | 59.45 | 60.32 | 61.12 | 61.44 | 61.73 | 61.98 |
| (17/241) | 62.43 | 62.42 | 62.56 | 62.67 | 62.73 | 62.75 | 62.76 | 62.77 | 62.75 | 62.76 |
Among the isomerizations considered in Table 1 the reaction 1 requires some additional attention. For this system an unexpectedly large discrepancy has been found between the CCSD(T) results published recently\textsuperscript{117} and the available experimental data.\textsuperscript{120–123} While the CCSD(T) isomerization energy from Ref. 117 is 101.3 kJ/mol, the experimental result reads 89.1 kJ/mol. As argued in Ref. 117 this substantial difference of about 12 kJ/mol cannot be explained by effects such as the basis set incompleteness, core-valence correlation contributions, relativity or zero-point vibrational energy corrections. This led to the conclusion that the experimental uncertainty is the most likely source of the problem. However, it is worthwhile to analyze whether the post-CCSD(T) effects may explain the discrepancy. To this end we carried out additional CCSD(T) and SVD-CCSDT+ calculations using cc-pVQZ orbital basis set. We obtained $-0.77$ kJ/mol difference between CCSD(T) and SVD-CCSDT+ results for $N_{\text{SVD}} = 200$. This result is converged to within $0.01 - 0.02$ kJ/mol with respect to the size of the SVD subspace. Within the smaller cc-pVTZ basis set the analogous result reads $-0.56$ kJ/mol. To further minimize the finite basis set error we employed the two-point (cc-pVTZ/cc-pVQZ) Riemann extrapolation\textsuperscript{124} towards the complete basis set limit. This gives the final estimation of $-0.97$ kJ/mol for the difference between CCSD(T) and CCSDT isomerization energies of reaction 1. Clearly, this value is too small to explain the observed difference between theory and experiment, supporting the conclusions of Ref. 117. The example of reaction 1 also demonstrates the usefulness of the SVD-CCSDT+ method in computation of the “pure” post-CCSD(T) effects which are known to be difficult to reproduce accurately for polyatomic molecules.\textsuperscript{125}

Finally, let us consider the second group of isomerization reactions. The results obtained with SVD-CCSDT and SVD-CCSDT+ methods are given in Table 2. Since this group of reactions involves larger molecules, we additionally include results obtained for $N_{\text{SVD}} = 180$ and $N_{\text{SVD}} = 200$. In general, the picture drawn from the data presented in Table 2 is analogous as discussed above. In all cases, with $N_{\text{SVD}} = 160 - 200$ the SVD-CCSDT+ results are essentially converged to within $0.01 - 0.02$ kJ/mol. Taking other sources of error
into account one can estimate that the difference with respect to the exact CCSDT method is, on average, smaller than 0.1 kJ/mol in this regime. At the same time, if the accuracy level of a few tenths of kJ/mol is sufficient, reliable results can be obtained with small SVD subspaces, \( N_{\text{SVD}} = 20 - 40 \). This is a considerable advantage of the SVD-CCSDT+ method over SVD-CCSDT as the latter is not trustworthy in the small \( N_{\text{SVD}} \) regime.

Last but not least, let us discuss the timings of the SVD-CCSDT+ calculations. As an illustrative example let us consider the product of reaction 15 (236 orbital basis set functions, 606 auxiliary basis set functions, 30 correlated electrons). For this system \( N_{\text{SVD}} = 120 \) is sufficient to converge the SVD-CCSDT+ results to within a few hundreds of kJ/mol. As a reference point, CCSD calculations for this system take approximately 520 min (converged within 18 iterations). Determination of the SVD subspace takes about 567 min, in a reasonable agreement with rough estimations made in Supporting Information. The SVD-CCSDT calculations for \( N_{\text{SVD}} = 120 \) take 1943 min (22 iterations). Therefore, the total computational cost of the SVD-CCSDT method is about five times that of CCSD for this molecule. Finally, the evaluation of the SVD-CCSDT+ correction takes ca. 815 min; by comparison, computation of the standard (T) correction takes about 300 min. Despite this overhead is non-negligible, we believe that this is a reasonable price to pay for a sizable reduction of the error in the final results. All timings reported in this paragraph were obtained using a single core of AMD Opteron™ 6174 processor without parallelization of the program execution and without exploitation of the point group symmetry.

4 Conclusions and future work

In this paper we have reported two novel developments in the field of the rank-reduced CCSDT theory. First, we have introduced a non-iterative energy correction, abbreviated as SVD-CCSDT+, added on top of the converged SVD-CCSDT result in order to approximately account for the triple excitations excluded from the parent SVD subspace. The working
formula for the correction has been derived by extending the Lagrangian formalism of Eriksen et al.\textsuperscript{71} with an additional assumption that the SVD subspace is closed under the action of the Fock operator. We have shown that in the limit of complete SVD subspace the value of the correction is rigorously equal to zero. In the opposite case of an empty SVD subspace the formula for the correction reduces to the well-known (T) method if sub-dominant terms that are at least quadratic in the cluster amplitudes are neglected.

The accuracy and computational efficiency of the proposed SVD-CCSDT+ correction has been assessed by studying a set of isomerization reactions involving small and medium-sized molecular systems. We have concluded that the non-iterative correction can fulfill two separate roles. If an accuracy level of a fraction of kJ/mol is sufficient, SVD-CCSDT+ correction significantly reduces the size of the SVD subspace that has to be employed in the iterative part of the calculations. Simultaneously, by adding the SVD-CCSDT+ correction the error due to the incompleteness of the SVD subspace can be reduced to levels considerably below 0.1 kJ/mol if the SVD subspace size is large enough. This levels of accuracy are usually impossible to achieve in practice solely with the SVD-CCSDT method. We have also presented representative timings of the SVD-CCSDT and SVD-CCSDT+ calculations, proving that the exact CCSDT results can be reproduced to within 0.1 kJ/mol with the computational cost only several times larger than required for the CCSD method. The SVD-CCSDT+ method retains black-box features of single-reference CC; the size of the SVD subspace remains the only additional parameter that has to be specified.

The second theoretical development introduced in this work is an algorithm for determination of the triples excitations subspace which is an alternative to the scheme given in Ref. 37. While the formalism proposed here is less general than the bidiagonalization strategy from Ref. 37, it scales rigorously as $N^6$, rather than $N^7$, with the system size. Therefore, despite a larger prefactor the proposed method is advantageous in applications to larger systems. Moreover, the new method comprises no iterative steps which eliminates accumulation of numerical noise and convergence problems one may encounter in iterative schemes.
As a final note, in the present work it has been demonstrated that the rank-reduced SVD-CCSDT+ method can reliably reproduce the exact CCSDT energetics with significantly decreased computational cost. The next important step is incorporation of quadruple excitation effects which become important at the 0.1 kJ/mol accuracy level. An economical way to take them into account is offered by non-iterative schemes such as CCSDT[Q]\textsuperscript{126–128} or CCSDT(Q).\textsuperscript{129–131} In particular, the latter method was found to systematically improve the quality of the results,\textsuperscript{132} in comparison to both CCSD(T) and CCSDT, at a reasonable computational cost. Nowadays the CCSDT(Q) method is often regarded as the "platinum standard" of the electronic structure theory,\textsuperscript{133} by analogy to the "gold standard" CCSD(T), and is a member of composite schemes routinely applied, e.g., in \textit{ab initio} computational thermochemistry.\textsuperscript{134–140} Unfortunately, incorporation of the (Q) correction in the present rank-reduced framework is not straightforward as its computational costs scale as $N^9$ with the system size if no approximations are introduced. This leads to a question whether by extending the rank-reduced CC formalism to the quadruply excited amplitudes one can reduce the scaling of the (Q) correction to a more manageable $N^7$ level, on par with the SVD-CCSDT+ theory. The answer to this question is affirmative and details of the procedure will be reported in a separate publication.

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Supporting Information Available

The following file is available free of charge via the Internet at http://pubs.acs.org:

- **plus-supp.pdf**: derivation of the non-iterative method for determination of the SVD subspace described in Sec. 2.1, numerical verification of the scaling of the SVD-CCSDT+ method, additional numerical results confirming the conclusions of Sec. 3.2, Cartesian coordinates of molecular geometries used in Sec. 3.3, and statistical error measures for results presented in Sec. 3.3.

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Graphical TOC Entry

\[
\begin{align*}
&\text{SVD-CCSDT} \\
&\quad t_{ij}^{\alpha\beta} = t_{\alpha\beta} t_{\gamma\delta} t_{\delta\gamma} t_{\gamma\delta} t_{\gamma\delta} \\
&\quad \downarrow \\
&\text{SVD-CCSDT+} \\
&- \left( v_{\alpha}^{\beta} \right)^{-1} \left( t_1 + t_2 H_{\alpha\beta} v_2 \right) v_{\beta}^{\alpha} H \\
\end{align*}
\]

< 0.1 kJ/mol error wrt. exact CCSDT
iterative $N^6$ + non-iterative $N^7$ cost
Supporting Information: Near-exact CCSDT energetics from rank-reduced formalism supplemented by non-iterative corrections

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1 Non-iterative determination of the SVD subspace

In this document we introduce an alternative method of obtaining the SVD subspace of triple excitations. In contrast to the algorithm introduced in Ref. 1, the new method is a one-step non-iterative procedure that has a rigorous $N^6$ scaling with the system size. However, it is applicable at present only to the approximate triples amplitudes given by Eq. (5) in the main paper.

In general, for any approximate $t_{abc}^{ijk}$ amplitudes tensor, the SVD subspace can be found by first forming the following symmetric square matrix

$$X_{ai,bj} = t_{ikl}^{ac} t_{jkl}^{bd}$$ (1)

and finding its eigenvectors corresponding to the largest eigenvalues. This is a consequence of the fact that for any rectangular matrix $M$, its left singular-vectors coincide with the eigenvectors of the normal matrix $MM^T$. While the diagonalization of the $X_{ai,bj}$ matrix scales as $O^3V^3$ and hence can be obtained efficiently, the cost of assembling the matrix $X_{ai,bj}$ is proportional to $O^4V^4$ if no additional simplifications are made. However, we show that for the $(2)t_{abc}^{ijk}$ amplitudes, defined by Eq. (5) in the main paper, the cost of this step can be reduced down to the level of $N^6$ (from now on, we drop the superscript $(2)$ from $(2)t_{abc}^{ijk}$ for brevity sake). To this end, one must first eliminate the three-particle energy denominator $\epsilon_{abc}^{ijk}$ that effectively prevents any factorization of the formula (1). For this purpose we employ the discrete Laplace transformation (LT)

$$(\epsilon_{ij}^{abc})^{-1} = \sum_{g} w_g e^{-t_g (\epsilon_i^a + \epsilon_j^b + \epsilon_k^c)}$$ (2)

where $\epsilon_i^a = \epsilon_i - \epsilon_a$, $t_g$ and $w_g$ are the quadrature nodes and weights, respectively, and $N_g$ is the quadrature size. This technique was originally introduced by Almlöf to get rid of the two-particle energy denominator in the MP2 theory, but it was subsequently employed in
other electronic structure methods,4–9 including CCSD(T).10 The problem of optimal choice of the quadrature nodes and weights has also been extensively discussed in the literature; for the purposes of this work we employ the min-max quadrature proposed by Takatsuka et al.11–13 The number of quadrature points in Eq. (2) is independent of the system size, i.e. \( N_g \propto N^0 \).

In a straightforward application of the LT technique the formula (2) has to be inserted twice into Eq. (1). This leads to the quadratic dependence of the computational costs on the number of quadrature points. While this would not change the ultimate scaling of the method it would significantly increase the prefactor. To avoid this problem we recall an elementary formula

\[
\frac{1}{\epsilon_{i}^{acd}} \frac{1}{\epsilon_{j}^{bcd}} = \frac{1}{\epsilon_{i}^b - \epsilon_{i}^a} \left( \frac{1}{\epsilon_{i}^{acd}} - \frac{1}{\epsilon_{j}^{bcd}} \right),
\]

(3)

where we have temporarily assumed that \( \epsilon_{i}^a \neq \epsilon_{j}^b \). Generalization to the degenerate case \( \epsilon_{i}^a = \epsilon_{j}^b \) shall be presented shortly. The advantage of this formula is that the product of two three-particle denominators is no longer present and a single application of the LT technique is sufficient. By rewriting the triple amplitudes as \( t_{ijk}^{abc} = (\epsilon_{ijk}^{abc})^{-1} \Gamma_{ijk}^{abc} \), inserting Eqs. (2) and (3), and after some rearrangements, Eq. (1) assumes the form

\[
X_{ai,bj} = \sum_{g} w_g e^{-t_s \epsilon_{i}^a} - e^{-t_s \epsilon_{j}^b} \Gamma_{ijkl}^{acd} \Gamma_{jkl}^{bcd} e^{-t_s (\epsilon_{k}^c + \epsilon_{l}^d)}, \quad \text{for } \epsilon_{j}^b \neq \epsilon_{i}^a.
\]

(4)

The case of degenerate orbital energy differences can now be resolved by analytically taking the limit \( \epsilon_{j}^b \rightarrow \epsilon_{i}^a \). This leads to a separate expression for the remaining elements

\[
X_{ai,bj} = \sum_{g} w_g t_g e^{-t_s \epsilon_{i}^a} \Gamma_{ijkl}^{acd} \Gamma_{jkl}^{bcd} e^{-t_s (\epsilon_{k}^c + \epsilon_{l}^d)}, \quad \text{for } \epsilon_{j}^b = \epsilon_{i}^a.
\]

(5)

The formulas (4) and (5) show that the matrix \( X_{ai,bj} \) can be obtained as a weighted sum
of simpler quantities in the form

\[ x_{ai,bj} = \Gamma_{iikl}^{acd} \Gamma_{jkl}^{bcd} e^{-t_g(\epsilon^c_k + \epsilon^d_l)} \]  

(6)

where the three-particle denominators are no longer present enabling an efficient factorization. To improve the efficiency of the calculations we additionally employ the following decomposition of the doubly excited CCSD amplitudes

\[ t_{ij}^{ab} = V_{ai}^A s_A V_{bj}^A, \]  

(7)

which is obtained by diagonalization treating \( t_{ij}^{ab} \) as a symmetric \( OV \times OV \) matrix. The advantage of this formula is that the eigenvectors corresponding to eigenvalues below a certain threshold, i.e., \( |s_A| < \epsilon \), can be dropped. As demonstrated by Parrish et al.,\(^{14}\) for a fixed value of \( \epsilon > 0 \) the number of retained eigenvalues, denoted \( N_{\text{eig}} \) further in the text, scales linearly with the system size. The cost of computing the eigendecomposition is proportional to \( O^3V^3 \) which is acceptable from the present point of view. If necessary, this cost can be reduced with the help of an iterative Lanczos-type diagonalization method which targets only the dominant eigenpairs. However, this possibility has not been explored in the present work.

Consider the following fixed form of the \( \Gamma_{ijk}^{abc} \) tensor

\[ \Gamma_{ijk}^{abc} = \langle abc | [W, T_2] \rangle = (1 + P_{bj,ck}) (1 + P_{ai,bj} + P_{ai,ck}) \left[ t_{ij}^{ad} (ck|bd) - t_{ij}^{ab} (ck|lj) \right], \]  

(8)

which corresponds to the triples amplitudes obtained in the leading order of the perturbation theory. For simplicity, in the above formula we employ the standard two-electron integrals corresponding to the pure fluctuation potential \( W \). However, exactly the same working formulas hold for the \( T_1 \)-transformed Hamiltonian, \( \widetilde{W} = e^{-T_1} W e^{T_1} \). To cover this case it is sufficient to replace the conventional two-electron integrals \( (pq|rs) \) by their \( T_1 \)-transformed
counterparts, \((pq\tilde{r}s)\), see Sec. 2.1 in the main paper. To facilitate an efficient evaluation of Eq. (6) with \(\Gamma_{ijk}^{abc}\) given by Eq. (8) we define the following intermediate that is independent of the Laplace grid points

\[
B_{ai}^{QA} = B_{ae}^{Q} V_{ei}^{A} s_{A} - B_{mi}^{Q} V_{am}^{A} s_{A},
\]

and a handful of grid-dependent intermediates

\[
Z_{PQ} = B_{ai}^{P} B_{ai}^{Q} e^{-t \eta \epsilon_{k}}, \quad Y_{A}^{P} = B_{ai}^{P} V_{ai}^{A} e^{-t \eta \epsilon_{i}}, \quad W_{AB} = V_{ai}^{A} V_{ai}^{B} e^{-t \eta \epsilon_{i}},
\]

\[
I_{A}^{PQ} = B_{ai}^{QA} B_{ai}^{P} e^{-t \eta \epsilon_{i}}, \quad J_{AB} = B_{ai}^{PA} V_{ai}^{B} e^{-t \eta \epsilon_{i}}.
\]

Calculation of the above intermediates scales as \(\propto N^5\) or lower and it does not constitute a bottleneck. With help of these quantities \(x_{ai,bj}\) can be rewritten as a sum of only six topologically distinct terms

\[
x_{ai,bj} = x_{ai,bj}^{(1)} + x_{ai,bj}^{(4)} + x_{ai,bj}^{(6)} + (1 + P_{ai,bj}) \left[ x_{ai,bj}^{(2)} + x_{ai,bj}^{(3)} + x_{ai,bj}^{(5)} \right],
\]

where

\[
x_{ai,bj}^{(1)} = V_{ai}^{A} V_{bj}^{B} \left[ B_{ck}^{QA} e^{-t \eta \epsilon_{k}} B_{ck}^{PB} Z_{PQ} + I_{A}^{QP} I_{B}^{PQ} \right],
\]

\[
x_{ai,bj}^{(2)} = V_{ai}^{B} B_{bj}^{QA} \left[ Z_{PQ} J_{BA}^{P} + Y_{A}^{P} I_{B}^{PQ} \right],
\]

\[
x_{ai,bj}^{(3)} = V_{ai}^{B} B_{bj}^{QA} \left[ B_{ck}^{PB} e^{-t \eta \epsilon_{k}} B_{ck}^{QA} C_{A}^{P} + I_{A}^{QP} J_{P}^{B} \right],
\]

\[
x_{ai,bj}^{(4)} = B_{ai}^{PB} B_{bj}^{QA} \left[ Z_{PQ} W_{AB} + C_{A}^{P} C_{B}^{Q} \right],
\]

\[
x_{ai,bj}^{(5)} = B_{ai}^{QA} B_{bj}^{P} \left[ C_{B}^{Q} J_{BA}^{P} + I_{B}^{QP} W_{AB} \right],
\]

\[
x_{ai,bj}^{(6)} = B_{ai}^{Q} B_{bj}^{P} \left[ B_{ck}^{QA} B_{ck}^{PB} e^{-t \eta \epsilon_{k}} W_{AB} + J_{AB}^{Q} J_{BA}^{P} \right].
\]

The computational cost of the whole procedure is dominated by the fourth term, \(x_{ai,bj}^{(4)}\).
where the rate-determining step scales as $O^2 V^2 N_{\text{eig}} N_{\text{aux}}$. Let us compare this with the most expensive term in the CCSD equations, the so-called particle-particle ladder diagram, with the scaling proportional to $O^2 V^4$. As demonstrated in the next section, in practice it is reasonable to assume that $N_{\text{eig}} \approx V$. This means that the cost of evaluating $x^{(4)}_{ai,bj}$ is more expensive than a single CCSD iteration by a factor of $N_{\text{aux}}/V \approx 2 - 4$. To this one has to add that $x^{(4)}_{ai,bj}$ must be evaluated at each Laplace grid point and $3 - 5$ points are usually required for a sufficient accuracy. Therefore, the cost of assembling the complete $\mathcal{X}_{ai,bj}$ matrix is expected to be comparable to $5 - 15$ CCSD iterations, the exact ratio depending on the desired accuracy level. While this prefactor is substantial, the main advantage of the proposed method is that the scaling of this procedure is the same as of the CCSD theory and this ratio is guaranteed to approximately hold for arbitrarily large systems.
2 Parameters in the non-iterative SVD subspace determination

Table 1: Relative error (in parts per million) in the SVD-CCSDT correlation energy for the methane molecule (cc-pVTZ basis set) as a function of the eigenvalue threshold ($\epsilon$) and number of Laplace grid points ($N_g$). The reference results were generated with $\epsilon = 0$ and $N_g = 20$.

| $\epsilon$ | $N_g$ |
|------------|-------|
| $\epsilon_f$ | $N_{SVD}$ = 25 | $N_{SVD}$ = 50 | $N_{SVD}$ = 75 |
| $10^{-2}$ | 1314 | 138 | 4 | 307 | 202 | 234 | 267 | 52 | 49 | 13 | 7 | 1 |
| $10^{-3}$ | 1417 | 66 | 54 | 260 | 54 | 13 | 7 | 1 |
| $10^{-4}$ | 1425 | 66 | 54 | 260 | 54 | 13 | 7 | 1 |
| $10^{-5}$ | 1423 | 66 | 54 | 260 | 54 | 13 | 7 | 1 |

The method of non-iterative determination of the SVD subspace introduced in here depends on two parameters that control the accuracy. The first one, denoted $\epsilon$ further in the text, is the truncation threshold in Eq. (7). Eigenvalue-eigenvector pairs with $|s_A| < \epsilon$ are dropped from the expansion (7), reducing its length to $N_{\text{eig}}$. The second parameter ($N_g$) is the number of quadrature points in the Laplace transformation of the three-particle energy denominator, Eq. (2). In this section we determine values of these parameters which minimize the computational effort necessary to find the SVD subspace, but simultaneously...
Table 2: The same data as in Table 1 but for the formaldehyde molecule (cc-pVTZ basis set).

| $\epsilon$ | $N_g$ |
|---|---|
|   | 2 | 3 | 4 | 5 | 7 | 10 |
| $N_{\text{SVD}} = 50$ |
| $10^{-2}$ & 251 & 426 & 450 & 447 & 450 & 451 |
| $10^{-3}$ & 54 & 178 & 20 & 32 & 30 & 29 |
| $10^{-4}$ & 18 & 139 & 23 & 5 & 1 & 14 |
| $10^{-5}$ & 17 & 138 & 23 & 7 & 6 & $<0$ |
| $N_{\text{SVD}} = 100$ |
| $10^{-2}$ & 202 & 287 & 243 & 263 & 259 & 258 |
| $10^{-3}$ & 19 & 33 & 11 & 29 & 27 & 26 |
| $10^{-4}$ & 32 & 45 & 4 & 7 & 2 & 1 |
| $10^{-5}$ & 33 & 45 & 5 & 10 & 4 & $<0$ |
| $N_{\text{SVD}} = 150$ |
| $10^{-2}$ & 4 & 122 & 206 & 208 & 205 & 202 |
| $10^{-3}$ & 203 & 69 & 7 & 2 & 7 & 4 |
| $10^{-4}$ & 201 & 64 & 3 & $<0$ & 3 & 1 |
| $10^{-5}$ & 202 & 66 & 2 & $<0$ & $<0$ & $<0$ |

guarantee a satisfactory accuracy level in the final results.

To this end we carried out SVD-CCSDT calculations for a dozen or so polyatomic molecules. The SVD vectors were determined using the method described in the previous section with different values of the control parameters $\epsilon$ and $N_g$. For several fixed $N_{\text{SVD}}$ we then recorded the error in the SVD-CCSDT correlation energy as a function of $\epsilon$ and $N_g$. As reference values we employ SVD-CCSDT results obtained with $\epsilon = 0$, i.e. without truncation of the expansion (7), and for $N_g = 20$ Laplace quadrature points. This is sufficient to make the reference data essentially exact for the present purposes.

We present results for two representative systems: methane molecule (tetrahedral geometry with $R_{\text{C-H}} = 1.0838\,\text{Å}$) and formaldehyde molecule (planar $C_{2v}$ geometry with $R_{\text{C-H}} = 1.1005\,\text{Å}$, $R_{\text{C-O}} = 1.2105\,\text{Å}$, and $\theta_{\text{H-C-O}} = 121.92^\circ$). The results are presented
in Tables 1 and 2, respectively. For both molecules we provide results for three different SVD subspace dimensions, purposefully chosen to be small, moderate and large from the point of view of realistic applications. In the case of the large SVD subspace we demand that the error in the correlation energy resulting from approximations in Eqs. (7) and (2) does not exceed 100 parts per million (0.01%). We expect this level of accuracy to be sufficient in most applications. For small SVD subspaces the accuracy requirement can be less stringent and an error of about one part per thousand (0.1%) is acceptable.

By inspection of the results given in Tables 1 and 2 one concludes that the combination of the eigenvalue threshold $\epsilon = 10^{-3}$ with $N_g = 4$ Laplace grid points is sufficient to reach the prescribed accuracy levels in all cases. While in some examples less strict values of the control parameters give unexpectedly small errors, this is probably accidental and is not expected to hold for a broader range of systems. Therefore, we recommend to set $\epsilon = 10^{-3}$ and $N_g = 4$ as a default in the algorithm described above. These values of the control parameters were employed in all calculations reported in this work.
3 Numerical verification of the computational complexity

To study the computational complexity of evaluating the $\delta E_{T+}$ correction we carried out the calculations for linear alkanes $C_nH_{2n+2}$, where $n = 1, 2, \ldots, 8$ denotes the chain length. The geometries of all molecules were taken from Ref. 15. We employ the cc-pVDZ basis set together with the corresponding cc-pVDZ-RI density-fitting basis. For each molecule the SVD subspace size is equal to the number of virtual orbitals in the system ($N_{\text{SVD}} = V$), according to the recommendations from the main text. The computational timings are reported in Fig. 1.

![Figure 1](image_url)

Figure 1: Timings $\tau$ of the $\delta E_{T+}$ calculations for linear alkanes $C_nH_{2n+2}$ as a function of the chain length, $n$. The timings are given relative to the calculations for $n = 1$ (denoted by the symbol $\tau_1$) and the plot employs the doubly-logarithmic scale. The dashed black curve is a linear function $(6.37x - 1.55)$ fitted to the data points for $n = 3, \ldots, 8$. 


4 Further numerical verification of the condition (14)

Figure 2: Values of the $R$ coefficient, see Eq. (40) in the main paper, as a function of the SVD subspace size for the H$_2$O molecule ($C_{2v}$ symmetry group, $R_{O-H} = 0.9562\,\text{Å}$, $R_{H-H} = 1.5096\,\text{Å}$, cc-pVTZ basis set, $1s^2$ oxygen core orbital frozen). The black dashed lines are linear functions connecting two neighboring data points. The maximum size of the SVD subspace for this system equals to 212.
Figure 3: The same data as in Fig. 2, but for the NH$_3$ molecule ($C_3v$ symmetry group, $R_{N-H} = 1.0101$ Å, $R_{H-H} = 1.6173$ Å, cc-pVTZ basis set, 1s$^2$ nitrogen core orbital frozen). The maximum size of the SVD subspace for this system equals to 268.

Figure 4: The same data as in Fig. 2, but for the HCCH molecule (linear geometry, $R_{C-H} = 1.0613$ Å, $R_{C-C} = 1.2041$ Å, cc-pVTZ basis set, two 1s$^2$ carbon core orbitals frozen). The maximum size of the SVD subspace for this system equals to 486.
5 Cartesian coordinates of molecular geometries used in Sec. 3.3 of the main paper

All coordinates are given in Ångströms.

| Molecule | Atom | X (Å) | Y (Å) | Z (Å) |
|----------|------|-------|-------|-------|
| BH₃      | B    | 0.0000| 0.0000| 0.0000|
|          | H    | 0.0000| 1.1900| 0.0000|
|          | H    | 1.0306| −0.5950| 0.0000|
|          | H    | −1.0306| −0.5950| 0.0000|
| C₂H₂     | H    | 0.0000| 0.0000| −1.0613|
|          | C    | 0.0000| 0.0000| 0.0000|
|          | C    | 0.0000| 0.0000| 1.2041|
|          | H    | 0.0000| 0.0000| 2.2654|
| CH₄      | C    | 0.0000| 0.0000| 0.0000|
|          | H    | −0.6271| 0.6271| 0.6271|
|          | H    | 0.6271| −0.6271| 0.6271|
|          | H    | −0.6271| −0.6271| −0.6271|
|          | H    | 0.6271| 0.6271| −0.6271|
| CO₂      | O    | 0.0000| 0.0000| −1.1601|
|          | C    | 0.0000| 0.0000| 0.0000|
|          | O    | 0.0000| 0.0000| +1.1601|
| CO       | C    | 0.0000| 0.0000| −0.6508|
|          | O    | 0.0000| 0.0000| 0.4882|
| NH₃      | N    | 0.0000| 0.0000| 0.0000|
|          | H    | 1.0101| 0.0000| 0.0000|
|          | H    | −0.2845| 0.0000| −0.9692|
|          | H    | −0.2845| 0.8394| 0.4846|
|     |     |     |     |
|-----|-----|-----|-----|
| **F₂** |     |     |     |
| F   | 0.0000 | 0.0000 | 0.0000 |
| F   | 0.0000 | 0.0000 | 1.4111 |
| **H₂CO** |     |     |     |
| C   | 0.0000 | 0.0000 | −0.6204 |
| O   | 0.0000 | 0.0000 | 0.5925 |
| H   | 0.9360 | 0.0000 | −1.1986 |
| H   | −0.9360 | 0.0000 | −1.1986 |
| **H₂O₂** |     |     |     |
| O   | 0.0000 | 0.0000 | 0.0000 |
| O   | 1.4495 | 0.0000 | 0.0000 |
| H   | −0.1669 | 0.0000 | −0.9464 |
| H   | 1.6164 | 0.8747 | 0.3612 |
| **H₂O** |     |     |     |
| O   | 0.0000 | 0.0000 | 0.0000 |
| H   | 0.9562 | 0.0000 | 0.0000 |
| H   | −0.2354 | 0.0000 | −0.9268 |
| **HCN** |     |     |     |
| N   | 0.0000 | 0.0000 | 0.5944 |
| C   | 0.0000 | 0.0000 | −0.5726 |
| H   | 0.0000 | 0.0000 | −1.6371 |
| **HCNO** |     |     |     |
| O   | 1.1624 | −0.0095 | 0.0000 |
| C   | −0.0104 | −0.0420 | 0.0000 |
| N   | −1.2232 | 0.0984 | 0.0000 |
| H   | −1.8750 | −0.6671 | 0.0000 |
| **HF** |     |     |     |
| H   | 0.0000 | 0.0000 | 0.0000 |
| F   | 0.0000 | 0.0000 | 0.9152 |
| **N₂** |     |     |     |
| N   | 0.0000 | 0.0000 | 0.0000 |
| N   | 0.0000 | 0.0000 | 1.0981 |
|          |     |     |     |
|----------|-----|-----|-----|
| **HCO₂H** |     |     |     |
| C        | 0.4159 | 0.0922 | 0.0000 |
| O        | −0.2086 | 1.1230 | 0.0000 |
| O        | −0.1250 | −1.1409 | 0.0000 |
| H        | −1.0882 | −1.0190 | 0.0000 |
| H        | 1.5057 | 0.0155  | 0.0000 |
| **N₂O**  |     |     |     |
| N        | −1.7980 | 1.5224  | 0.0000 |
| N        | −0.9703 | 0.7222  | 0.0000 |
| O        | −0.1239 | −0.0961 | 0.0000 |
6 Statistical measures of the relative errors defined
in Sec. 3.3 of the main paper

Table 3: Statistical measures (in percent) of the relative error in the total SVD-CCSDT and SVD-CCSDT+ correlation energies with respect to the exact CCSDT method. The quantities $\bar{\Delta}$ and $\Delta_{\text{std}}$ are defined in the main text, Eqs. (42) and (43). The parameter $x$ defines the size of the triple excitation subspace, $N_{\text{SVD}} = x \times N_{\text{MO}}$, where $N_{\text{MO}}$ is the total number of orbitals in a given system.

| $x$  | SVD-CCSDT |          | SVD-CCSDT+ |          |
|------|-----------|----------|------------|----------|
|      | $\bar{\Delta}$ | $\Delta_{\text{std}}$ | $\bar{\Delta}$ | $\Delta_{\text{std}}$ |
| $\frac{1}{6}$ | −1.2970 | 0.5388 | −0.1632 | 0.0432 |
| $\frac{1}{3}$ | −0.5676 | 0.6710 | −0.1020 | 0.0453 |
| $\frac{1}{2}$ | −0.0855 | 0.1478 | −0.0637 | 0.0363 |
| $\frac{2}{3}$ | 0.0730 | 0.0936 | −0.0491 | 0.0293 |
| $\frac{5}{6}$ | 0.1166 | 0.0469 | −0.0391 | 0.0245 |
| 1 | 0.1135 | 0.0476 | −0.0321 | 0.0203 |
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